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No. 12.

STUDIES ON UREIDES.

PART 2.

THE CHEMISTRY OF TRIURET AND RELATED COMPOUNDS.

By

A. E. A. WERNER AND J. GRAY.

[Read March 26, 1946. Published separately July, 1946.]

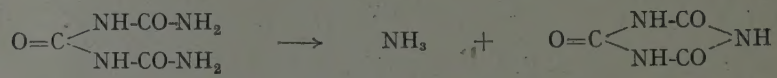
In a previous communication (1) it was shown that when equimolecular proportions of thionyl chloride and urea were refluxed biuret was obtained. Shortly afterwards Haworth and Mann (2), using a smaller molecular proportion of thionyl chloride, confirmed the formation of biuret, but reported the formation of the compound triuret, or carbonyl diurea, $CO(NH\text{-}CO\text{-}NH_2)_2$. Repetition of the reaction, as recorded in the present investigation, has confirmed the results of Haworth and Mann (*loc. cit.*), triuret being obtained in yields up to 30 per cent. of the theoretical. The failure to detect triuret in the original investigation may be traced to the fact that it is readily decomposed in alkaline solution into ammonia and cyanuric acid. This reaction constitutes in fact the most convenient method for the preparation of triuret; other methods described by Schmidt (3), Schiff (4), and Schittenhelm and Warnat (5) are either troublesome or give smaller yields. Haworth and Mann (*loc. cit.*) regarded the formation of biuret and triuret as involving primarily the deamination of urea; but, in view of the experimental evidence obtained by the writers (6) concerning the mechanism of the formation of allophanates by the action of thionyl chloride on carbamates, it is probable that an analogous mechanism is responsible for the formation of biuret from urea and cyanic acid, and the triuret is then formed by the addition of cyanic acid to biuret according to the following equation:—

$$O{=}C\begin{matrix}\diagup NH_2\\ \diagdown NH\text{-}CO\text{-}NH_2\end{matrix} + HN{=}C{=}O \longrightarrow O{=}C\begin{matrix}\diagup NH\text{-}CO\text{-}NH_2\\ \diagdown NH\text{-}CO\text{-}NH_2\end{matrix}$$

Such a mechanism would be in agreement with the observation of Bougault and Leboucq (7) that triuret is formed along with biuret when allophanic acid chloride is treated with ammonia.

Although, as reported by Haworth and Mann (*loc. cit.*), thiourea is not attacked by boiling thionyl chloride, we have found that it is readily decomposed by this reagent at 140°-145°C forming initially ammonia and thiocyanic acid together with cyanamide and hydrogen sulphide; further secondary reactions led to the formation of a mixture of ill-defined by-products.

Owing to the present rather inadequate and contradictory state of the chemistry of triuret, the work detailed below was undertaken to gain more precise data about its chemical behaviour. The melting point of triuret has been recorded as 231-232°C by Schiff (*loc. cit.*), as 227°C (with effervescence) by Haworth and Mann (*loc. cit.*), while Walters and Wise (8) maintain that triuret has no true melting point, the figure recorded as such being the temperature at which triuret was supposed to undergo deamination, cyclising to form cyanuric acid with the evolution of ammonia, according to the following equation:—



Our specimen of triuret darkened and underwent sudden decomposition at 230°C, but showed no appearance of fusion even when the temperature was raised to 250°C. This behaviour confirms the finding of Walters and Wise (*loc. cit.*) but further investigations showed, however, that the thermal decomposition of triuret cannot be represented as a mere deamination with the immediate formation of cyanuric acid as the sole non-volatile product. The detection of such by-products as ammonium cyanate and urea present in the sublimate formed on the cool sides of the test-tube, and biuret and ammelide present in the infusible residue, preclude this explanation. Cyanuric acid is quite stable up to about 300°C, and once formed would not subsequently decompose to yield the by-products above mentioned. In point of fact the triuret molecule undergoes complete disruption to give initially ammonia and cyanic acid, from which the final products are formed in a manner similar to that involved in the thermal decomposition of urea as described by E. A. Werner (9).

Since Schiff (*loc. cit.*) mentioned that triuret gives a faint biuret reaction, we have investigated the behaviour of triuret with copper salts in alkaline solution. According to our findings a violet coloration was produced when a concentrated alkaline solution of triuret was treated with only a *few drops* of dilute copper sulphate solution, but the addition of more copper sulphate solution produced a deep-blue colour, due to the formation of a copper complex compound with the triuret. This deep-blue solution was only stable for a few days. On standing black copper oxide was deposited and long acicular crystals of cyanuric acid separated from the now colourless solution. The formation of cyanuric acid is due to the slow decomposition of triuret in alkaline solution. The action of nitrous acid on triuret was next investigated and compared with the behaviour of biuret and acetamide. Although a suspension of triuret did not react with nitrous acid, even in the presence of a large excess of mineral acid, a solution of triuret in 50 per cent. sulphuric acid was found to react readily, with the evolution of nitrogen and carbon dioxide.

A certain amount of nitrogen was however fixed in the form of an ammonium salt, which was detected in the solution when the reaction was completed. This behaviour parallels that of biuret, and supports the constitution assigned to triuret. The initial reaction may be represented by the following equation:—

$$O{=}C\begin{matrix}\text{NH-CO-NH}_2\\ \text{NH-CO-NH}_2\end{matrix} + 2HNO_2 \longrightarrow 2N_2 + 2CO_2 + 2H_2O + O{=}C\begin{matrix}\text{NH}_2\\ \text{NH}_2\end{matrix}$$

The urea formed then reacts with nitrous acid in the manner described by E. A. Werner (10):—

$$O{=}C\begin{matrix}\text{NH}_2\\ \text{NH}_2\end{matrix} + HNO_2 \longrightarrow N_2 + 2H_2O + HNCO \begin{matrix}\xrightarrow{(a)} NH_3 + CO_2\\ \xrightarrow{(b)} N_2 + CO_2 + H_2O\end{matrix}$$

Reaction (a), the hydrolysis of cyanic acid, is responsible for the formation of the ammonium salt.

Haworth and Mann (*loc. cit.*) have directed attention to an unexpected alternation in certain properties shown by biuret, triuret, and the next two homologues in the series, namely the substances described in the literature as 'tetrauret' and 'carbonyl dibiuret.' The following tabulation is taken from their paper:—

	M.P. °C	Solubility in cold water	Biuret reaction
$NH(CONH_2)_2$	190 (decomp).	Moderately soluble	Deep red colour
$CO(NHCONH_2)_2$	231 (,, ,,).	Slightly soluble	Very faint colour
$NH(CONHCONH_2)_2$	186 (,, ,,).	Readily soluble	Intense violet colour
$CO(NHCONHCONH_2)_2$ . . .	235 (,, ,,).	Almost insoluble	No coloration

This unexpected alteration in the specified properties, and in particular the remarkable closeness in the melting points recorded for the two pairs of substances *biuret* and *tetrauret*, and *triuret* and *carbonyl dibiuret*, would seem to warrant a more detailed investigation in order to amplify the very meagre knowledge of the chemistry of the two substances tetrauret and carbonyl dibiuret, and thereby establish definitely whether these two latter compounds do actually exist.

The first reference to the substance tetrauret is contained in a paper by Thiele and Uhlfelder (11), who described its preparation by the action of ammonia on allophanic azide; they recorded its melting point as 186°C, and stated that it could be distinguished from biuret by its crystalline form, its greater solubility in water, and its violet colour with alkaline copper sulphate. This reaction has been recently reinvestigated by Lipschitz (12), who treated allophanic azide with ammonia under varied experimental conditions, but in every case he could only isolate the normal amide, biuret, which was identified by chemical analysis and by mixed melting point with an authentic specimen of biuret. In no experiment was a significantly different product formed which could be claimed as the substance tetrauret.[1] An alternative method for the preparation of tetrauret was described by Davis and Blanchard (13), who warmed an aqueous solution of biuret and nitrobiuret to a temperature of about 80°C. They stated that the nitrobiuret decomposed in the aqueous solution

[1] The above reaction would seem to be unique, because carbamic azide gives urea, and *not* biuret, on treatment with ammonia, according to the work of Thiele and Uhlfelder (*loc. cit.*).

to yield nitroamide and dicyanic acid, which then combined with unchanged biuret to give a substance which they identified as tetrauret. Their identification was only based on the fact that its properties, e.g. melting point and biuret reaction, were similar to those of the substance described by Thiele and Uhlfelder (*loc. cit.*). No analytical data was given, no mixed melting point determination was made, and no attempt was made to prepare any derivatives by which the compound might have been more definitely characterised. We have repeated the experimental procedure describd by Davis and Blanchard (*loc. cit.*), but have been unable to isolate any product of the reaction other than biuret, which was identified by mixed melting point determination with an authentic specimen of biuret and by analysis of its nitrogen content. In no experiment was a substance obtained corresponding to tetrauret. It is thus evident that the substance described in the literature as tetrauret has not been obtained by either of the methods purporting to describe its preparation, and, until further experimental evidence is produced to the contrary, the existence of such a substance must be regarded as extremely doubtful.

The original preparation of the substance known as carbonyl dibiuret was described by Schmidt (*loc. cit.*), who obtained it in small yield by heating biuret with phosgene for twelve hours at 60°C in a sealed tube. Schmidt did not record any melting point for his product, but recorded analytical data corresponding to the required formula, $C_5H_8O_5N_6$. He further mentioned that the compound was more soluble in water than triuret (which he had also prepared at the same time by reacting urea with phosgene), and that when nitrous fumes were passed for a short time into a suspension of the compound in warm water, carbon dioxide was evolved and on cooling crystals of urea nitrate were deposited together with cyanuric acid. Finally he described the formation of the insoluble compound $C_5H_8O_5N_6 \cdot 3HgO$ formed upon the addition of mercuric nitrate to a hot aqueous solution of the same substance. Schiff (*loc. cit.*) a few years later claimed to have obtained the same substance, again in small yield, by heating urea with phosgene in toluene solution for two days at 100°C in a sealed tube. He characterised the substance by recording its melting point as 235°C with decomposition, and remarking that the substance gave a feble biuret reaction, but he did not include any analytical data concerning the compound. The meagre data presented by Schmidt and Schiff has not been verified by any recent workers, and taken by itself it is not sufficiently conclusive to put the existence of the substance described as carbonyl biuret beyond possible doubt. In view of the very probable non-existence of the so-called tetrauret it is reasonable to seek for an alternative interpretation of the observations of Schmidt and Schiff. The isolation of cyanuric acid as one of the products of the action of nitrous acid on the supposed carbonyl dibiuret is highly significant. It is very difficult to account for the formation of cyanuric acid as a normal product of such a reaction; since, for example, triuret does not yield cyanuric acid on treatment with nitrous acid although these two substances should be closely related. The only reasonable explanation would seem to be that the cyanuric acid is already present in the substance treated with the nitrous acid, i.e. the supposed carbonyl dibiuret is merely a mixture of the two compounds triuret and cyanuric acid. Such a mixture would account for the

properties attributed to carbonyl dibiuret, e.g. its melting point and its apparent greater solubility in water (since cyanuric acid is appreciably more soluble in water than triuret). Furthermore the analytical figures given by Schmidt, namely C=25.74, H=3.75 and N=36.37%, are equally in agreement with those of a mixture of cyanuric acid and triuret in the ratio 1:3, which requires C=25.7, H=3.5 and N=36.4%. Finally it should be noted that cyanuric acid and triuret are stable substances whose formation might readily be expected in the techniques described by Schmidt and Schiff for the preparation of the supposed carbonyl dibiuret, and in this connection it is of particular significance that the so-called carbonyl dibiuret is converted quantitatively into cyanuric acid if it is heated with excess phosgene, as was shown by Schmidt himself (*loc. cit.*). We are therefore led to the conclusion that the non-existence of the two substances described in the literature as tetrauret and carbonyl dibiuret is the true explanation of the unknown factor supposed to be responsible for the remarkable alternation in properties to which attention was directed by Haworth and Mann (*loc. cit.*). This conclusion would seem to receive a certain measure of support from the fact that no derivatives of either 'tetrauret' or 'carbonyl dibiuret' have been prepared, whereas well characterised derivatives of triuret have been described, e.g. 1:7 dimethyl triuret[1] has been prepared by Fischer (14) by reacting *sym*-dimethyl urea with phosgene, and a series of benzylidene derivatives has been obtained by Bellavita (15).

EXPERIMENTAL.

Interaction of urea and thionyl chloride. A mixture of dry, finely powdered urea (30 g.) and thionyl chloride (13.5 c.c.) was heated on a water-bath for 2½ hours with occasional vigorous shaking. While still warm unreacted thionyl chloride was removed by evacuation of the flask; the orange-yellow solid mass left was extracted with distilled water (150 c.c.) at 70°C, and an undissolved residue of triuret was collected (Weight=6.4 g. Decomposition point 230°C). The filtrate deposited on cooling monohydrated biuret in flat plates which in vacuum desiccator became anhydrous. (Weight=13.2 g. M.P. 185°C). On recrystallisation from ethyl alcohol the M.P. was raised to 190°C, being unchanged on mixing with an authentic specimen of biuret. The crude triuret was freed from traces of cyanuric acid by recrystallisation from boiling water, from which it was deposited in the form of small glistening needles. (Weight=5.6 g. equivalent to 23 per cent. of the theoretical yield. Found N=38.3 per cent. $C_3H_6O_3N_4$ requires N=38.4 per cent.) A repetition of the experiment gave biuret (13.8 g.=53.6 per cent. of the theoretical) and triuret (7.4 g.=30.5 per cent. of the theoretical).

Action of heat on triuret. Triuret (1.0 g.) was heated in a clean dry test-tube. Traces of ammonia gas started to be evolved at 175°C, being detected by its

[1] Biltz (16) has also prepared this substance, but prefers to represent it as the 1:5 dimethyl isomeride.

characteristic odour and the blueing of moist litmus paper held over the mouth of the test-tube. At 232°C the whole mass suddenly decomposed with copious evolution of ammonia gas, but no apparent fusion occurred. A brownish residue remained in the test-tube, which dissolved readily in caustic soda; this solution gave strong positive tests for the presence of biuret, ammelide, and cyanuric acid. The sides of the test-tube were covered with a white deposit, which was found to contain small amounts of cyanuric acid, ammonium cyanate, and urea.

Action of heat on cyanuric acid. Cyanuric acid (0.5 g.), previously dehydrated by heating at 110°C, was maintained at a temperature of 250°C for 30 minutes. There were no obvious signs of decomposition, and tests for the presence of ammonium cyanate were negative.

Colour reaction of triuret with alkaline copper sulphate. To a saturated solution (5 c.c) of triuret in caustic soda (10%) one drop of copper sulphate solution (5%) was added. A clear violet coloration developed similar to that given by biuret. Upon the gradual addition of further amounts of copper sulphate solution the solution assumed a deep-blue colour similar to that given by ammonia and amines. Five c.c. of copper sulphate solution was added to a solution (20 c.c.) of triuret (0.23 g.) in caustic soda; excess copper hydroxide precipitate was filtered off, and the deep-blue solution was left to stand at room temperature in a stoppered cylinder for a period of two weeks, during which a black precipitate of copper oxide settled out together with long white crystals These crystals were identified as cyanuric acid. Weight=0.237 g. equivalent to 92% of the theoretical yield, assuming that one molecule of triuret gives rise to one molecule of cyanuric acid dihydrate, $(HNCO)_3 2H_2O$.

Interaction of biuret and nitrobiuret in aqueous solution. Nitrobiuret (1.4 g.) and biuret (1.2 g.) were dissolved in warm water (50 c.c.) When effervescence had ceased the solution was evaporated down to a volume of 10 c.c. A crystalline material separated. Weight=0.98 g., M.P. 175°C (Davis and Blanchard (*loc. cit.*) reported weight =0.60 g. M.P. 178°-180°C). Recrystallisation from ethyl alcohol gave a product M.P. 188°C, not depressed by mixture with an authentic specimen of biuret. Found N=40.6 per cent. $C_2H_5O_2N_3$ requires N=40.8 per cent., whereas a compound of the formula of ' tetrauret,' namely $C_4H_7O_4N_5$, would require N=37.0 per cent.

Action of nitrous acid on triuret, biuret, and acteamide. Acetamide (0.059 g.) biuret (0.05 g.) and triuret (0.073 g.) were dissolved in 50 per cent. sulphuric acid (4 c.c.), and treated in a nitrometer with an aqueous solution (2 c.c.) containing one milligram molecular proportion of sodium nitrite. After thirty minutes the volume of gas evolved was noted, and the gas analysed; the carbon dioxide content was determined by noting the decrease in volume after treatment with a saturated solution of potassium hydroxie, and the amount of nitric oxide was determined by absorption in a concentrated solution of potassium permanganate. All volumes

were reduced to N.T.P., and the actual results (averages of three experiments) are tabulated below:—

	Volume of Gases in c.c.		
Substance	CO_2	NO	N_2
Acetamide	0	3.10	11.20
Biuret	14.50	1.20	18.45
Triuret	10.15	3.6	15.95

Interaction of thiourea and thionyl chloride. Dry, finely powdered thiourea (7.6 g.) was heated with thionyl chloride (13 c.c.) in a sealed tube at 140°C for 1½ hours. Vigorous reaction occurred with the formation of an orange-yellow product. On opening the tubes gas under considerable pressure was released (in one case the tube was completely disintegrated with great explosive force.) The residue was extracted with boiling water (75 c.c.) and filtered while hot. An insoluble yellow amorphous powder remained. Weight =3 g. Insoluble in organic solvents. On heating deposit of sulphur forms on the walls of the test-tube, and a dark-brown infusible residue remains. The filtrate gives a positive test for the presence of thiocyanate and sulphide, and upon neutralisation with sodium hydroxide a white precipitate is formed, which redissolved on warming, giving a yellow solution.

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No. 13.

EVIDENCE FOR A MITOTIC HORMONE: OBSERVATIONS ON THE MITOSES OF THE EMBRYO-SAC OF *FRITILLARIA IMPERIATIS*

By

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PLATES 8, 9, AND 10.

[Read NOVEMBER 27, 1945. Published Separately JULY, 1946].

IN the year 1894 I came across peculiar modifications of form in resting and mitotic nuclei of the endosperm of *Fritillaria imperiatis*. A short account of some of them was given in a paper read before the Royal Irish Academy in November, 1895.

In the study of the preparations made for these observations remarkable examples were found in which the successive stages of mitosis followed one another in faultless sequence in the nuclei embedded in the protoplasmic lining of the embryo-sac (Pl. 8, Figs. 1-9).

To investigate the problem as to how such an orderly arrangement was brought about a considerable number of preparations were made. The material consisted of young seeds from the green capsular fruits of *F. imperialis* collected when the seed measured approximately 5 x 3 x 2 m.m. These were fixed in 95% alcohol. Quick penetration and fixation of the cytoplasm and the nuclei of the embryo-sac were secured by the puncture of the seed with a needle as it was submerged in the alcohol.

Some of the seeds after fixation were split with a scalpel or razor parallel to the two flat sides of the seed, cutting through the embryo-sac down almost to the funiculus. The sides of the seed were then prized apart and under 50%-70% alcohol the membranous protoplasmic lining was dissected out from the nucellus. In this way good preparations of the lining were obtained in the form of two dished ovals cohering by their fold on the funicular side. After transference through several changes of water they were stained in dilute Delafield's Haematoxylin. When

the stain, judged by direct microscopic examination in water was judged to be sufficiently intense, the linings were washed, dehydrated, cleared in oil of cloves, and mounted in balsam.

Such preparations of material fixed in the early stages of growth of fertilized ovules afforded wonderful examples of the orderly sequence of the successive stages of mitosis distributed in the cytoplasmic lining of the embryo-sac (Pl. 8, Figs. 1-9).

The nuclei are very uniformly scattered in the protoplasm. In the earlier stages there are no cell-walls separating them. Many of them may be undergoing mitosis. The fact that the nuclei in each stage of mitosis form parallel bands in the film forces itself upon the observer. Each band is composed of 1, 2, 3 or more parallel lines of nuclei in the same stage of nuclear division, prophase, metaphase, anaphase and telophase. Generally the prophase band is composed of 4 or 5 lines of prophase nuclei, the aster band of one or two aster lines, the metaphase, anaphase and diaster bands of one or two lines each, and the telophase band of four or five lines merging finally into a wide region occupied by resting interphase nuclei. The correspondence between the succession of the stages with their spatial distribution is challenging.

Plate 8 shows microphotos of nine successive stages of mitosis from successive bands from one of these films.

Like many other embryo-sacs the uninucleate condition of the embryo-sac of *F. imperialis* appears to give rise to a coenocyte with 8 nuclei. The secondary nucleus of the sac is formed by the fusion of two of these nuclei. By successive mitosis this fusion-nucleus (the secondary nucleus of the embryo-sac) gives rise to the numerous nuclei of the endosperm. These are distributed through the growing protoplasm of the enlarging embryo-sac. Meanwhile the liquid contents of the sac coalesce to form a large central vacuole and by their rapid accumulation reduce the protoplasm to a thin film, or pellicle, lining the sac.

(Plate 10, Fig. 1) shows a longitudinal section of young seed cut at right angles to its median plane which passes through the centre of the sac and the axis of the funiculus. This section shows the scattered nuclei in the more or less distorted lining, which has drawn away from the surrounding nucellus. Part of this lining is seen as a continuous sheet of cytoplasm, and parts of it are seen in section. In the latter parts the nuclei appear as enlargements on the protoplasmic film. Possibly in the living state the protoplasm, being spongy and vacuolate, completely encloses the nuclei. Fixation and dehydration processes have probably been responsible for this change. Elsewhere the nuclei are seen against a more or less continuous sheet of cytoplasm. It may be noticed that in this, as in many similar preparations of this stage, a succession of consecutive stages of mitosis from the base to the apex of the sac is apparent. The earliest stages, viz., resting and prophase nuclei, are at the base of the sac, aster, metaphase, anaphase, and diaster stages are seen in its middle, while at its apex, in the region round the embryo, dispirem, telophase and completely resting nuclei only are found.

Such a distribution of mitotic stages suggests that the initiating cause of mitosis travelled from the position of the final stage represented to that of the earliest one in the sequence observed. Furthermore it may be noted this very complete graduation of all the mitotic stages is only found before the development of the later com-

partmented structure, and while all the nuclei are equally exposed to substances dissolved and diffusing in the cell-sap filling the embryo-sac.

It is not till after the embryo-sac has become greatly enlarged, and many hundred nuclei have been formed by successive mitoses, that separating cell-walls are formed in the protoplasmic lining film. Plate 9, Fig. 3 shows the beginning of this change, as seen from the inside of the embryo-sac vacuole. At first only the radial walls are formed mapping out considerable regions of the film into polygonal stalls round each nucleus; but apparently leaving each nucleus for some time accessible to the dissolved substances in the vacuole of the sac. Graded mitoses in these open cells are very evident in Plate 9, Fig 4. This state of things is also rendered very apparent in transverse sections of the sac, made at this time or a little later, Plate 10, Fig. 2. Here we see the lens-shaped cross-section of the sac, in which the antifunicular fold is lined by a single layer of cells, separated from one another by tenuous radial protoplasmic films and plates, but with no defined cell-wall shutting them off from the central vacuole. The funicular fold, on the other hand, is more or less filled with thin-walled parenchyma; but even in this parenchyma the cells adjoining the vacuole are often open to it, and in sectioning their nuclei are frequently displaced into it.

The grading of the mitotic stages in these open cells, whether they belong to the funicular parenchyma, or to the antifunicular layer, is in harmony with the view that they are accessible to a diffusing, initiating, vacuolar substance, or hormone. Plate 10, Fig. 3 showing six consecutive cells isolated from the antifunicular layer is a fortunate and striking example.

In these transverse sections of the sac, while the endosperm is still non-septate, or composed for the greater part of a single layer of cells enclosing the central vacuole and opening into it (Plate 10, Fig. 2), the location of the recording mitotic stages indicates that the starting point of the diffusing hormone, while near the apex of the sac, is often situated on the side remote from the funiculus and that the hormone seems to pass downwards towards the base of the sac and inwards towards the chalaza and funiculus. In the cases observed the point of entry was not exactly opposite to the funiculus, but a little displaced to one side of the sac (Plate 10, Fig. 2). Hence it is that in these transverse sections of the sac the telophases are spread more on one side of the sac than on the other. Consequently we must imagine the front of the diffusing hormone to be oblique to the median plane of the sac.

As long as the lining is not subdivided into cells the axes of the mitoses are parallel to the outer wall of the embryo-sac (Plate 9, Figs. 1 and 2) and, as nuclear division proceeds, cell-walls begin to be formed at right angles to and crossing the mitotic spindles (Plate 9, Figs. 3 and 4). The resulting nuclei thus come to lie between these recently formed radial walls. These radial walls make connection with the outer wall of the sac, and each nucleus thus finds itself in a polygonal cell closed on one side by the continuous cell-wall on the outside of the embryo-sac, but on the inner side open to the vacuole of the sac (Plate 10, Fig. 2). If the cell-wall of the embryo-sac is growing rapidly the following mitoses like their predecessors have their axes parallel to the wall of the sac (Plate 9, Figs. 2 and 4) exemplify this result. If, on the other hand, expansion of the sac in a tangential

direction is forbidden, increase in a radial direction is favoured, and accordingly the axes of new mitoses are oriented radially (Plate 10, Figs. 2 and 3). These radially oriented spindles lay down cell-walls in a tangential plane which close the cells previously opening into the vacuole and shut into the vacuole one of every pair of resulting nuclei. The process is repeated, till the tissue of the endosperm increased layer by layer, is complete.

The independent mitosis of closed cells (Plate 9, Figs. 5 and 6) affords no evidence that they are initiated by a substance diffusing and spreading through the tissue of which they are part. This independence of divisions occurring in nuclei located in closed cells, coupled with the fact that nuclei, which are *not* thus cut off from the vaucole by cell-walls never fail to show co-ordination with one another, seems to me to afford strong evidence that these co-ordinated mitoses owe their initation to contact of a dissolved diffusing substance which is arrested or much delayed by continuous cell-walls or their protoplasmic lining. Furthermore we cannot assign the co-ordination to the action of mitogenetic rays produced by one mitosis and stimulating its neighbours; for the experiments which are supposed to have demonstrated the existence of these rays show that they are effective on nuclei located within closed cells of a tissue, and no co-ordination of the mitoses of these is recorded.

From the observations recorded it is evident, that some relationship must exist between the rate of change of one mitotic stage into those which follow and the velocity of the movement of the initiating substance. If its rate of spread were high all the nuclei would receive the stimulus almost simultaneously, and the mitotic stages throughout the whole protoplasmic film would almost synchronise. On the other hand, if the movement of the hormone were *very* sluggish, a long time would elapse between its successive contacts with the nuclei in its path and the mitosis of the first recipient would be over and complete before that of the next was started. Thus if we know the time intervals between the stages of mitosis and their distances frim one another we can estimate the rate of movement of the hormone or initiating substance. Several observers have recorded the times taken for the complete process of mitosis and for the intervals between its successive stages. As might be expected the rates are dependent on the temperature.

The following figures for the duration of mitosis are quoted from Introduction to Cytology by L. W. Sharp, 3rd Edition, 1936. Nuclei in the staminal hairs of Tradescantia 30 minutes at 45°, 75 minutes at 25° and 135 minutes at 10°. Martens (La cellule 38, 1927) found the time from the beginning of prophase to the end of telophase was 78 to 110 minutes. M. and W. Lewis (1917) recorded that complete mitosis in the mesenchyme of the chick was accomplished in 70-180 minutes. So we may take it that at air temperatures mitosis is completed in one or two hours.

In the protoplasm on the wall of the embryo-sac of *Fritillaria imperialis* and of *Helleborus orientalis* the distance from the early prophase stages of the mitoses described in this paper to the final stages of telophase measures 1.0 mm. to 1.4 mm. Hence according to the suggestion put forward the hormone must have travelled this distance in one or two hours.

It is of interest to note that the speed of diffusion of various colloidal dyes into water held in a gelatin gel varies from 0.1 mm. for Erythrosin (mol. wt 880) to 0.34

mm. for Chrysoidin (mol. wt 212). While the diffusion speed of solutions of various chlorides varies from 1.0 mm to 1.4 mm per hour. (Pflanzenphysiologisches Praktikum Theil II p. 3, by L. Brauner, 1932). If these figures are applicable to the hormone of mitosis, it would appear that it must be a substance in the crystalloidal and not in the colloidal state.

While one is generally impressed with the regularity of the parallel lines formed by the successive stages of mitosis in the coenocytic film of the embryo-sac, these lines sometimes become zig-zag and even greatly flexed forming sinuous curves; so that in extreme cases tongues of metaphase and even anaphase may penetrate the bands of prophase nuclei. With the ageing of the endosperm and its more complete septation these irregularities become more frequent, so that we may find groups of prophases surrounded by later stages and even sporadic mitotic nuclei isolated in a tissue, the majority of whose nuclei are resting. It seems legitimate to assign the bulk of these irregularities to the resistance opposed to the equable spreading of the hormone by the multiplying cells and membranes. Even in earlier stages the orderly march of diffusion must often be interfered with by accidental blows on the walls of the fruit and local temperature changes. The latter will not only speed up or retard diffusion but may also, influence the rate of mitotic change.

Preparation of pieces of the endosperm film containing all the nine stages figured in Plate 9 uniformly present roughly equal numbers of each. This indicates that each of the stages here figured occupies an interval of time approximately equal to the total duration of mitosis divided by nine; i.e., in a mitosis lasting 110 minutes (*cf.* Martens above) the dividing nucleus spends approximately 12 minutes in each of these stages.

In conclusion, I would like to acknowledge my indebtedness to Sir Frederick W. Moore, Sc.D., who on many occasions supplied me with all stages of developing fruits of *F. imperialis*. I have also to express my thanks to Mr. Joseph Murray for his assistance in producing the photographic records in this paper.

DESCRIPTION OF PLATES.

PLATE 8.

Figs. 1-9. Microphotographs of nine stages of mitosis, selected from one preparation of the protoplasmic lining of the embryo-sac of *Fritillaria imperialis*. x 820.

PLATE 9.

Fig. 1, *Helleborus orientalis*. Nuclei and mitoses in the protoplasmic lining of the embryo-sac. No separating walls have yet appeared. Prophase mitotic stages are seen below, metaphases across the middle of the field and anaphases above. x 140.

Fig. 2, *Fritillaria imperialis*. Nuclei and mitoses in the protoplasmic lining of the embryo-sac. No separating cell-walls have yet appeared. Prophases are seen

at VI o'c in the field, metaphases just below the diameter, anaphases above the diameter and telophases in the upper quarter of the field. x 75.

Fig. 3, *Fritiallaria imperialis.* Nuclei and mitoses in the protoplasmic lining of the embryo-sac. Separating radial walls between the mitoses are seen in the upper half of the field. The same sequence of mitotic stages are found from below upwards as in Figs. 1 and 2. x 50.

Fig. 4, *Fritillaria imperialis.* Nuclei and mitoses in the protoplasmic lining of the embryo-sac. Separating cell-walls are seen between the mitoses. Sections at right angles to the lining film of protoplasm at the same time show that there are no cell-walls separating these mitoses from the central vacuole of the embryo-sac. The same sequence of prophase, metaphase, anaphase and early telophase from below upwards is observable. x 150.

Fig. 5, *Fritillaria imperialis.* Nuclei and mitoses in tissue of growing nucellus. The mitoses are sporadic among the resting nuclei. No harmonizing control is apparent. x 150.

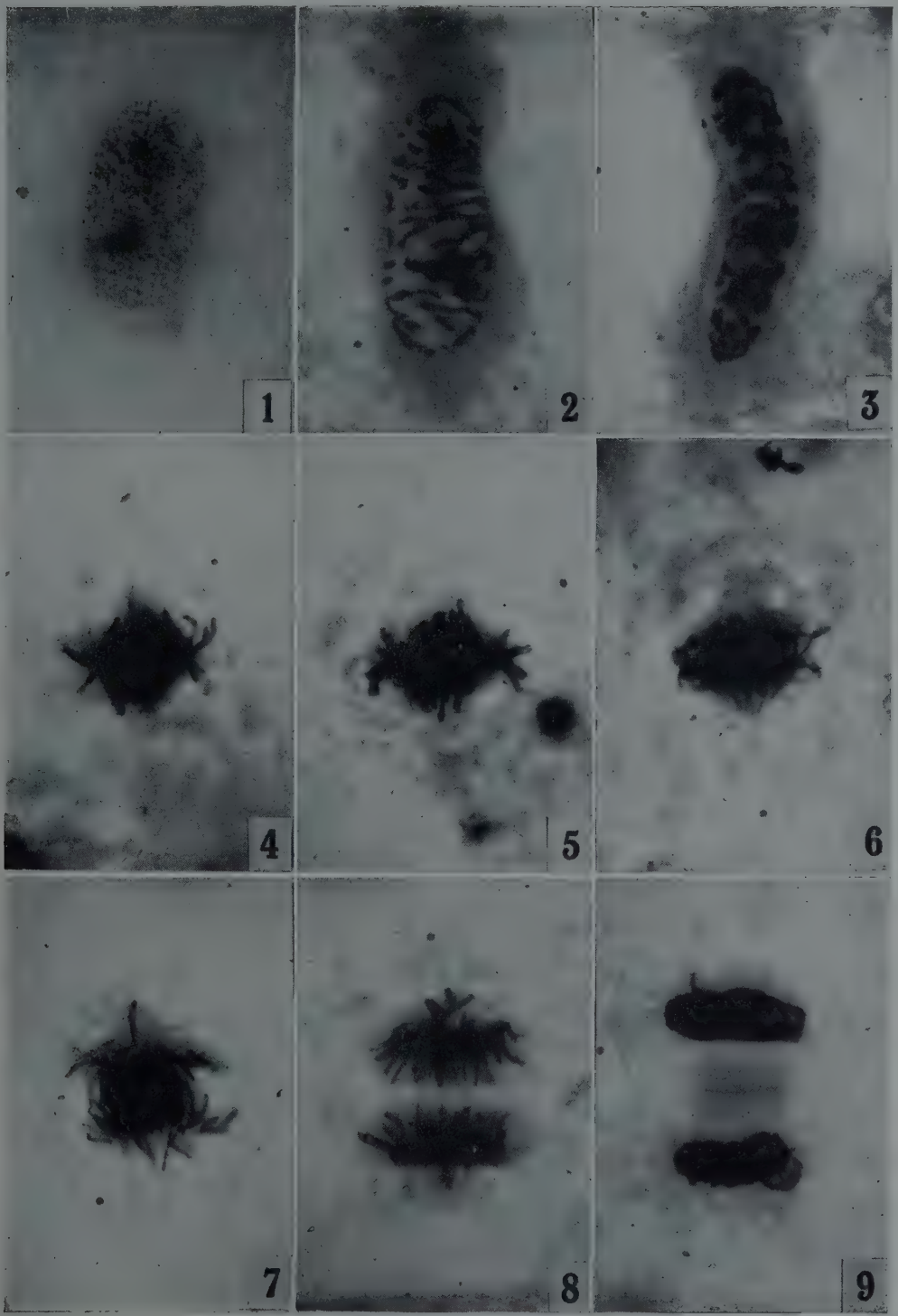
Fig. 6, *Fritillaria imperialis.* Nuclei and mitosis in tissue of growing nucellus. Single diaster is not supported by earlier stages. It may be noted that at least 30 minutes elapse between the earliest prophase and the diaster stage. Hence if a hormone evoked this mitosis it has failed in 30 minutes to traverse the walls enclosing the adjacent cells still exhibiting interphase nuclei. x 200.

Plate 10.

Fig. 1, Microphotograph of a tangential longitudinal section of the embryo-sac of *Fritillaria imperialis.* Successive stages of mitosis are exhibited by the endosperm nuclei—the prophases at the base and subsequent stages upward throughout the sac in regular sequence. A slow movement of the hormone downwards in the sac is indicated. x 40.

Fig. 2, Transverse section—reconstructed from two adjacent microtome sections—of the embryo-sac of *Fritillaria imperialis.* The endosperm, which is massive in the funicular fold of the sac, is only one cell thick on its radial sides and in the antifunicular fold. No cell-walls cut off the cavities of this single layer of cells from the large central vacuole, and it may be seen that the successive contacts of the diffusing vacuole hormone have been able to produce the usual orderly mitotic sequences in these cells, and to harmonize the sequences of the stages in the cells of the two opposite sides. x 50.

Fig. 3, Microphotograph of six adjacent cells dissected from the wall of a transverse section of an embryo-sac of *Fritillaria imperialis.* The sequence of mitotic stages indicates the passage of the mitotic hormone from right to left. x 250.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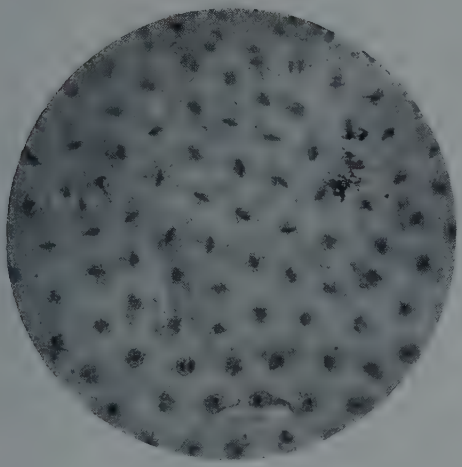

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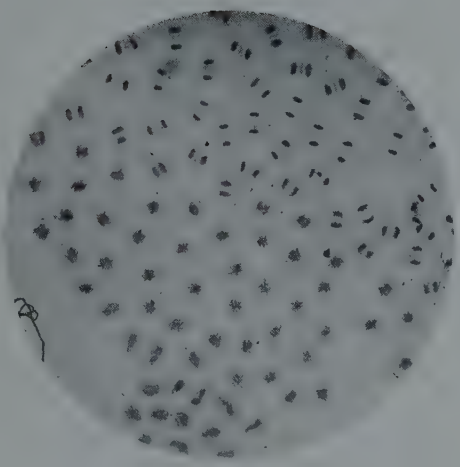

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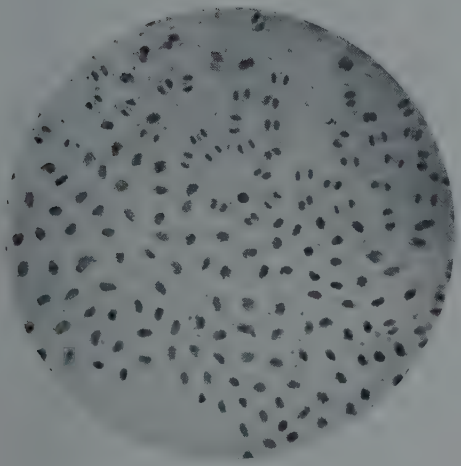

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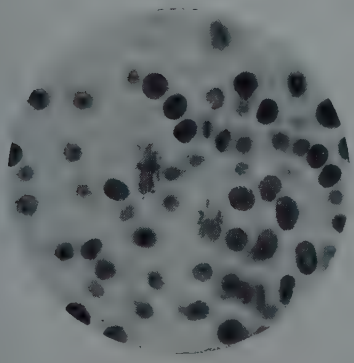

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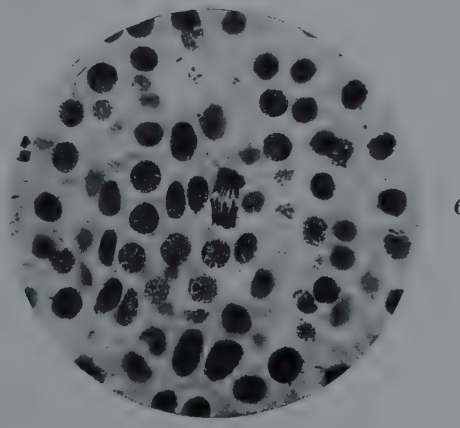

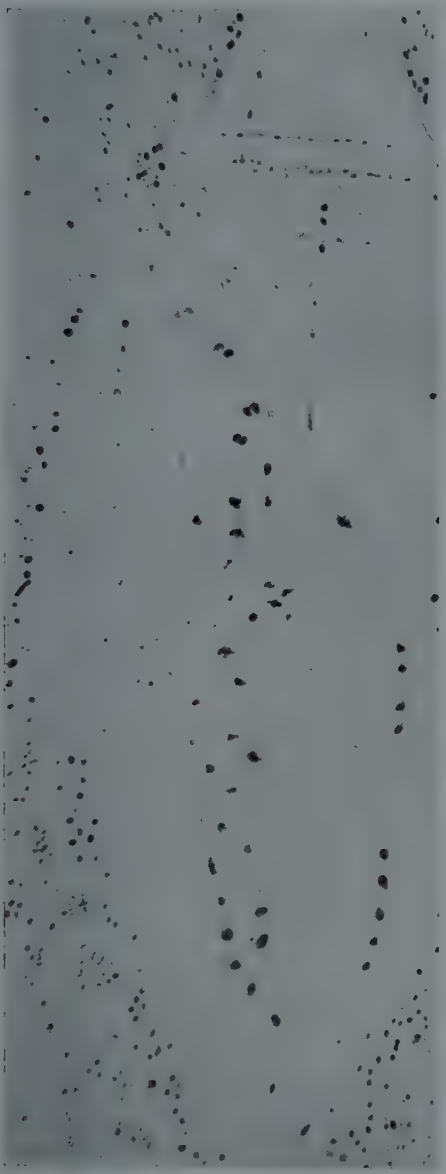

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No. 14.

THE OCCURRENCE OF NICKEL AND MAGNETITE IN SOME IRISH SERPENTINES, IN CONJUNCTION WITH A MAGNETIC SURVEY.

By D. W. Bishopp, A.R.S.M.

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Introduction.

The serpentine of Slishwood, Co. Sligo, was the subject of a paper by E. T. Hardman with supplementary notes by Prof. Hull, published in the Proceedings of the Royal Dublin Society for 1883. In this, Hardman drew attention to a high content of magnetite (up to 15%) in the rock, and to a percentage of nickel reaching up to 2.5% in some partial analyses. Two complete analyses showed 1.00% and 1.25% nickel oxide, but the exact localities are not precisely specified.

For some years very low grade nickel-silicate ores assaying less than 2% metal have been worked in the Ural districts of Svedlovsk, Oufaley, and Orsk, U.S.S.R. A deposit of similar character has recently be described from Dillon, Montana, U.S.A.

Early in 1942 the Geological Survey carried out an investigation of the Slishwood and other serpentine occurrences in Counties Sligo and Leitrim. Samples were taken for analysis, and the magnetic profiles across some of the occurrences were determined with a Watts vertical variometer. In 1943 a further set of samples was analysed from the belt of serpentine rocks which occurs on the flank of the Croagh Patrick range between Westport and Louisburgh, Co. Mayo. This is the south-westerly extension of the same range of metamorphic and intrusive rocks—the Slieve Gamph or Ox mountains—which are traversed by the Slishwood serpentine south of Lough Gill, Co. Sligo.

The object of this investigation was primarily to determine whether there were any points where concentration of metallic ores might be expected.

Descriptions of Occurrences, and Magnetic Characteristics.

(1) *Slishwood* (1″ Map No. 55, 6″ Sheet Sligo No. 21, 25″ Sligo XXI, 2, 6, 10.) This occurrence, which forms the subject of Hardman's paper, is the most extensive of the serpentines in this area. It is intrusive into quartzose and granitic gneisses; it has a width of 150 metres at its northern end in Lough Gill, and about

110 metres at the southern limit of the outcrop, which is 2,500 metres long. At this point, magnetic observations have indicated its extension for at least another 400 metres southward below the supervening cover of Carboniferous sediments.

Along the centre of this belt the serpentine is dark green to black, hard, dense, and homogeneous in texture. It is nowhere exposed in contact with the gneiss, but toward the edges becomes lighter in colour, more granular, and of a banded appearance. It tends to split along planes parallel to the foliation of the gneiss, giving a pseudo-stratified appearance. At its southern end these planes dip at 70° to 90°W; at the northern end at 45° to 50° in the same direction.

In hand specimens the rock shows small crystals and fine threads of magnetite fairly evenly distributed. Thin talcose bands occur, and narrow strings of cross-fibre chrysotile asbestos are common near both margins, and are best seen near the western edge of the south end of the serpentine belt. Here, between 5 and 12 metres to the east of the contact (which is not exposed) with the gneiss, a width of 2.5 m. contains 75 bands of chrysotile from 1-3 mm. and rarely up to 5 mm. thick.

Thin sections and polished specimens of the fresh rock give rather meagre information. They show scattered opaque dust and crystals of magnetite in a comparatively clear serpentine ground mass of characteristically low birefringence. There may be a fine network of small crystals of magnetite together with crystals of opaque mineral up to 2 mm. diameter, which may also be magnetite, but tests for chromite or ilmenite have not yet been carried out. Hardman records the percentage of magnetite as varying from 2-15, adding that the higher concentration occurs in samples from the west of the serpentine belt. Nine analyses of typical examples from Slishwood in the course of the present investigation yielded an average of 8.33% total iron, equivalent to 8.0% magnetite, the values ranging between 7.4 and 10.7% magnetite.

Preliminary traverses (Nos. 70, 58, 9, 18, 31) on the accompanying map were made across the belt with observations at 10 m. intervals, and were continued over the gneiss in either direction, in spite of difficulties due to terrain. Readings over the gneiss as far as 150 m. from the serpentine boundaries were far from constant, and these variations were attributed to disseminated magnetite, which was later found there in some quantity. A normal value for the vertical component of the magnetic field was obtained over gneiss near the southern end of the belt, and over the adjoining limestone; both these formations yielded constant readings which agreed within the limits of accuracy required. The profiles drawn for the traverses across the serpentine were very irregular and of little value.

On Traverse 31 a completely different anomaly was encountered, and an attempt to measure it in detail by readings at 5 m. intervals was made, but proved impracticable. Within certain areas marked on the maps, larger anomalies were encountered which must be treated as distinct from the ordinary mass. These anomalies were in places of both signs and outside the limits of measurement of the instrument used (—15,000 γ to + 15,000 γ.) In spite of their intensity they were of very small extent, thus indicating the disturbance to lie close to the surface. Trial profiles of one anomaly were uninterpretable. In consequence the remaining traverses were made in order to outline areas where similar anomalies occurred, the grid-spacing being approximately 30 m. while readings were taken at 20 m. intervals and shortened to 10 m. as soon as abnormal readings were encountered.

Based on the Ordnance Survey by permission of the Minister for Finance.

Over the belt of alluvium which covers the serpentine near its southern end, only a few traverses were made, principally in order to check the width of the magnetic formation.

The magnetic survey showed the anomaly over most of the serpentine belt to be up to +1,000 γ, being higher near both boundaries than at the centre. This seems rather small in view of Hardman's analyses; but samples broken off and brought near the variometer produced only very small effects. The great erratic anomalies may have some relationship with the strike of the serpentine belt, since for example the areas they occupy (the sign being disregarded) are lens-shaped although very irregular, with their longitudinal axes approximately in the line of strike. These areas, as can be seen from the map, were only found near the boundaries on either side, and not down the centre, which consistently seems to be the only homogeneous part of the belt of dyke. In some of these areas the magnetic field, as traced out by a compass needle, was similar to the field produced by a North-South horizontal dipole of about 10 m. separation whose South pole pointed North. However at another area the field was similar to that of a single South pole.

The horizontal component of the field is also very disturbed and in places a compass needle is deflected 180°. The vertical field anomalies at points only a few metres apart may differ in sign and value by over 30,000 γ. The samples collected in these hyper-anomalous areas showed no very marked difference in character from those obtained elsewhere.

Several traverses were made across the serpentine areas at Aghamore, Stonepark, and Pollboy (q.v.). The anomaly here was of the same order as that generally encountered at Slishwood; but no very high values were recorded.

(2) *Aghamore.* (6″ Sligo No. 21). With the exception of one small outcrop interpolated by McHenry on Hardman's map the occurrence had not previously been recorded, and the variometer observations are responsible for its extension.

Here a belt of serpentine runs along the foot of a steep scarp of gneiss. The limits of the belt are not evident through heavy drift and talus, but outcrops were observed over a distance of 400 m., and the belt appears to continue to the north-east and south-west. The contact rocks on the south-west are coarse quartzitic gneisses which dip north-west at 85°. The north-western contact is somewhat problematical. The serpentine lies very close to the fault-junction between the Carboniferous limestone and the metamorphic rocks, but whether it abuts against the fault or is separated from it by a band of gneiss has not been determined. One traverse run across the serpentine belt indicated a width of about 80 m. In appearance the serpentine is similar to that at Slishwood, but it is slightly darker in colour and shows no banding nor chrysotile veins.

(3) *Stonepark.* (6″ Leitrim No. 14/1.2). Serpentine here occurs in a belt running E.S.E.-W.N.W. along the edge of an alluvial flat. The rock is exposed over a length of 400 m., and passes under thick alluvium to east and west. Two traverses were run across this belt and showed its width to be about 100 m. The

serpentine resembles that at Slishwood, but is somewhat darker in colour and less talcose. It shows similar pseudo-bedding, but no well-defined banding is evident.

(4) *Pollboy.* (6″ Leitrim No. 11/1.) Here a narrow belt of serpentine lies between gneiss and Carboniferous limestone. It is divided from the latter by a fault with which appears to be associated a copper mineralization in the limestone. The serpentine runs in a north-east to south-west direction, is about 450 metres long, and is cut off by faults at each end. Its width as shown by two traverses is about 70 metres. The rock is similar in appearance to that at Stonepark and Aghamore.

(5) *Clew Bay Area.* (6″ Mayo Nos. 87, 88. 1″ No. 74.) No magnetic observations have been made here. The analyses are given in a succeeding paragraph; the samples were taken from a chain of occurrences extending twelve miles from east to west. These are steep-sided dykes with a certain degree of continuity, intrusive into gneisses, schists, and quartzites of the Croagh Patrick range.

ANALYSES OF SERPENTINES.

No.	Locality	Nickel as NiO.		Total Iron as Fe_2O_3		vt. Magnetite
		% *		% *		%
1.	Slishwood, see 25″ map	0·30	av: 0·257 =0·202% Ni.	8·5	av: 8·1 =7·8 Fe_3O_4	8·2
2.	Slishwood	0·26		7·9		7·6
3.	Slishwood	0·08 †		7·8		7·5
4.	Slishwood	0·26		7·7		7·4
5.	Slishwood	0·26		8·3		8·0
6.	Slishwood	0·29		8·0		7·7
7.	Slishwood	0·26		7·8		7·5
8.	Slishwood	0·24		8·0		7·7
9.	Slishwood	0·28		11·1		10·7
10.	Pollboy	0·34		6·3		6·05
11.	Aghamore	0·26		8·0		7·7
12.	Stonepark	0·26		8·0		7·7
13.	Clew Bay area, Co. Mayo (exact locality undefined)	0·21		8·0 not included in average.		

No.	Locality		Nickel as NiO.		Total Iron as Fe_2O_3		vt. Magnetite
			% *		% *		%
14.	Mayo 88/1.	1a. ...	0·36		7·0		6·7
15.		1b. ...	0·20		7·5		7·2
16.		1c. ...	0·20		6·9		6·6
17.		1d. ...	0·20		8·3		8·0
18.	Mayo 88/3	2a. ...	0·26		7·6		7·3
19.		2b. ...	0·36	av: 0.298	8·5	av: 8·1	8·2
20.	Mayo 87/4	3a. ...	0·46		9·7		9·3
21.		3b. ...	0·20	=0·235%Ni.	12·8	=7·8 Fe_3O_4	12·3
22.		3c. ...	0·29		9·3		8·9
23.	Mayo 87/4	4a. ...	0·42		6·7		6·4
24.		4b. ...	0·24		7·2		6·9
25.		4c. ...	0·20		5·6		5·4
26.		4d. ...	0·39		9·0		8·65
27.		4e. ...	0·39		7·6		7·3

* Analyst: The State Laboratory. A preliminary determination of nickel on samples 1–12 in the undried condition was also made by Mr. T. Murphy (G.S. Laboratory) who found values between 0·15% and 0·27% NiO average 0·201% NiO, which is in good correspondence with the State Laboratory figures for dried samples.

†0·08 checked by repetition.

Summary and Comments.

Chemical Composition. The serpentines which form the subject of this short investigation would not, in the light of modern petrology, be held to be anything but dykes derived from some ultra-basic parent, and intruded into the metamorphic complex which is here almost certainly pre-Cambrian. The contact of the Slishwood serpentine with the Lower Carboniferous rocks which overlie it has not been adequately exposed, but its pre-Carboniferous age is inferred.

The average content of nickel in the Sligo-Leitrim group of serpentines is 0.202%, with 8.1% total iron estimated as Fe_2O_3 equivalent to 7.8% magnetite. The Mayo group contains a little more nickel, 0.235% average, while the iron content calculated as magnetite is also 7.8%, the average of 14 samples being identical with that of 12 from the Sligo-Leitrim group. Individual assays do not deviate very much from the mean in most cases.

It is improbable that all the iron is present as magnetite, but the evidence of thin sections and magnetic separation suggests that most of it is in this form. If so, the content in 12 samples from Slishwood ranged between 6.05% and 10.7% as against Hardman's 2% to 15 %, the individual content being close to 8% in most cases. The Curie point corresponding to magnetite has kindly been determined by Dr. J. H. J. Poole.

It has nowhere been possible to confirm the high contents of nickel reported by Hardman, but no specimen has been found which does not contain nickel. This may be due to the greater reliability of the modern dimethyl-glyoxime analysis, which is specific for this metal. A sampling error may however occur through using weathered specimens in which the nickel tends to become slightly concentrated.

It is interesting to note a parallel example in the early work of Bonney (1891) on the Lizard Serpentines (Cornwall), which indicated up to 0.6% Ni; this was subsequently reduced by Flett and Hill to the lower figure of 0.15%. The content of 0.2% Ni given in our Irish analyses compares with those from the Cornish area, and with those cited by Clarke (Data of Geochemistry, U.S.G.S.). A similar occurrence has recently been described from Dillon, Montana,—a low grade nickel silicate deposit in which the nickel content of serpentine and related rocks ranges between 0.15% and 1.25%. In the case of the serpentines of New Caledonia, Blanchard (1944) has pointed out that the average content of nickel, judged from samples taken all over the island regardless of proximity to commercial deposits, is 0.3%.

The Irish analyses shows a fair degree of uniformity in total nickel and iron content. The Mayo group is derived from a more or less continuous chain of serpentine dykes twelve miles in length; and a distance of 60-70 miles intervenes between these and the Sligo-Leitrim group at the north eastern extremity of the Slieve Gamph range of hills.

No appreciable quantity of sulphide or arsenide minerals has so far been detected in this preliminary investigation; the magnetite fraction obtained by pulverising the rock and by magnetic separation does not appear to carry nickel, which only becomes soluble on fusion of the rock with alkali. This seems to show that it was present as a primary silicate in the ultra-basic parent rock, as in the occurrence of New Caledonia, the Urals, and Dillon, Montana.

There is no evidence as yet that would indicate the presence of the highly magnetic oxide of iron and nickel, Trevorite, which was described from South Africa in 1921, or of the suggested new nickel silicate allied to talc which is the subject of a paper by the late F. C. Partridge (Trans. G.S. S. Africa, 46, 1943); but it would be well to bear these possibilities in mind in future work. The possible occurrence of chromite has not been studied.

There is some confusion in Hardman's original paper regarding the asbestos veins which are termed 'chrysolite' or tremolite,' although Hull accepted the latter determination very doubtfully. This asbestos is more correctly, chrysotile, as Kilroe points out in G.S. Memoir 55; but comparatively few of the bands exposed at the surface contains fibres of commercial flexibility or length.

From the economic point of view, the concentration of nickel and magnetite in these rocks is not sufficient to admit of their commercial recovery by present-day processes. The Orsk smelter of the Urals appears to handle an average ore containing in the undried condition as little as 1% Nickel; the average slag loss has been given as 0.25% and sometimes as low as 0.15%. The New Caledonian nickel-silicate ore may have a metal content of 5%, but slag losses range from 0.50-0.60% nickel. In the Ural plants the ore is smelted in blast furnaces with gypsum and other fluxes to form a matte. If it had been possible to sustain Hardman's figures, the extraction of Irish nickel on these lines might have been considered; but the average nickel content of the Slieve Gamph serpentines appears to be approximately equal to the slag loss at the Orsk smelter. The results of investigations carried out by the Anaconda Copper Co. on the comparable but somewhat richer deposits at Dillon, Montana, have not been disclosed.

Magnetic characterstics of the Slishwood dyke.—Some magnetite is dissiminated in the gneiss bordering the serpentine; but a survey of the vertical component of intensity over this body shows:—

(a) a general anomaly about 1,000 γ higher than in the surrounding country, and

(b) a number of very localized erratic anomalies of extremely high intensity without regard to sign. These are not related to the quantity of magnetite present, but rather to the orientation and polarity of the magnetic units which are scattered throughout the rock.

Mr. T. Murphy, the physicist attached to the Survey, observes that the general low anomaly over the serpentine, so far as could be ascertained, is in accordance with the earth's field. Hence it is inferred that this anomaly was produced solely through induction by the earth's field in material whose susceptibility was greater than that of the adjoining rocks. This susceptibility is not known, hence a comparison between theoretical and practical results can not be made.

The very local readings of great intensity, which are definitely referred to polarization, appear to be due to material close to the surface. With one or two exceptions all occur where the overburden is very thin, and the majority near a cliff-face or upjutting outcrop. The exceptions are covered by drift of undetermined thickness.

Mr. Murphy suggests that magnetite in the original dyke would, on cooling below the Curie point of about 600°C, acquire a polarity in accordance with the earth's field then prevailing. In this form the coercive force would be quite low and the rock as a whole would show little or no polarity. (It is clear, however, that the molecular regrouping caused by the subsequent hydration of an original peridotite to serpentine would have unpredictable effects). It is also suggested that the strong local polarization occurring chiefly near the highest points of the serpentine may have been produced at a much later period by the intense fields of lightning flashes. The general anomaly of course persists well beneath the cover of Carboniferous rocks at the south extremity of the dyke whose ultimate length is unknown. There appear to be too many factors unknown at present, to permit of a convincing explanation.

I am indebted to the State Chemist for the determinations of nickel and iron in the foregoing analyses. The variometer observations, geological field work and associated laboratory investigations were carried out by Mr. M. A. Cunningham of the Geological Survey and Mr. T. Murphy of the Emergency Research Bureau who kindly provided the variometer. Permission to reproduce Ordnance Survey maps on which the work was based, and to publish this paper, is by courtesy of the Ministers for Finance and for Industry and Commerce, respectively.

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No. 15.

THE MAGNETIC PROPERTIES OF THE SERPENTINE DEPOSITS IN THE SLISHWOOD GAP, COUNTY SLIGO, IRELAND.

By

W. E. SEEDS, M.Sc. AND J. H. J. POOLE, Sc.D.

[Read January 30, 1945. Published separately August 29, 1946].

Plate II.

Introduction.

During 1942 and 1943 the Geological Survey of Ireland undertook a partial magnetic survey of the serpentine deposits near Slishwood, County Sligo, Ireland, since it has been known for some time that the serpentine deposits of County Sligo and County Mayo contain a small percentage of nickel, which might in the future have commercial possibilities, (1). The survey was conducted with a Watt's Vertical Variometer. Very large and rapid variations in the vertical magnetic field were observed, and the nature of these variations indicated that the serpentine must be fairly strongly permanently magnetised, the direction of magnetisation being sometimes nearly in the opposite direction to the existing Earth's field. Tests with a magnetometer on hand specimens confirmed this hypothesis, and showed that specimens from different localities differed greatly in intensity of magnetisation.

It was accordingly decided to conduct more accurate measurements on the magnetic properties of the serpentine, using specimens whose original position and orientation were known. It was hoped by this means to gain some knowledge of the nature, magnitude, and direction, of the original polarising magnetic field. As the number of oriented specimens was limited, some tests were also made on unmarked specimens.

The nature and general characteristics of the Slishwood serpentine is discussed in a recent paper by D. W. Bishopp, Director of the Irish Geological Survey (1). A sketch map (Fig. 1.) showing the geological character of the district and the locality from which the specimens were obtained is reproduced from this paper. The ser-

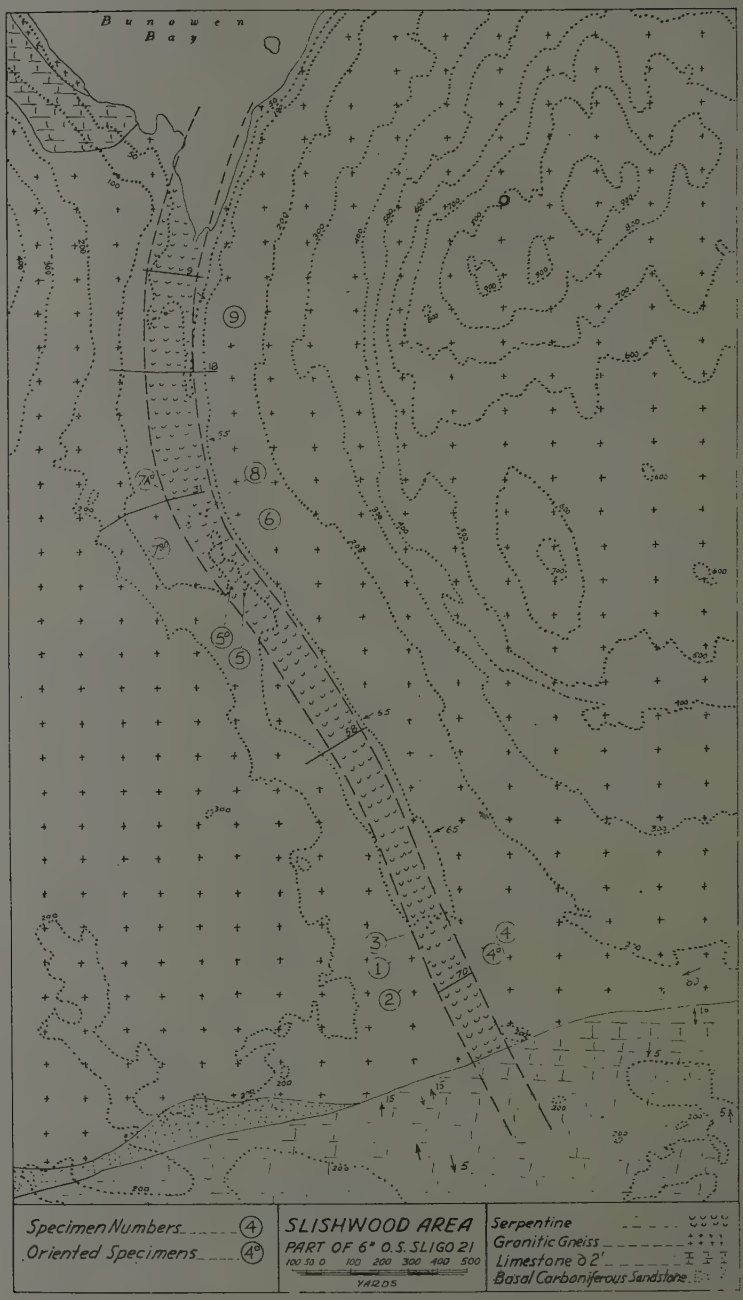

FIG. 1.

Based on the Ordnance Survey by permission of the Minister for Finance.

pentine deposits consist of a narrow belt varying in width between about 150 and 110 metres, and about 2500 metres in length. At the northern end, the outcrop disappears under the waters of Lough Gill, and at the southern end under the Carboniferous limestone. Magnetic observations have shown that the serpentine extends for at least another 400 metres southward below this Carboniferous cover, which presumably indicates that the serpentine is at least pre-Carboniferous in age. It may be remarked that the serpentine belt now lies at the bottom of a steep-sided stream valley, and this fact introduces some difficulty in explaining the origin of the permanent magnetisation of the serpentine, as will be seen later.

EXPERIMENTAL ARRANGEMENT.

The apparatus, used for determining the intensity and direction of the original permanent magnetisation of the serpentine, is shown schematically in Fig. 2. It

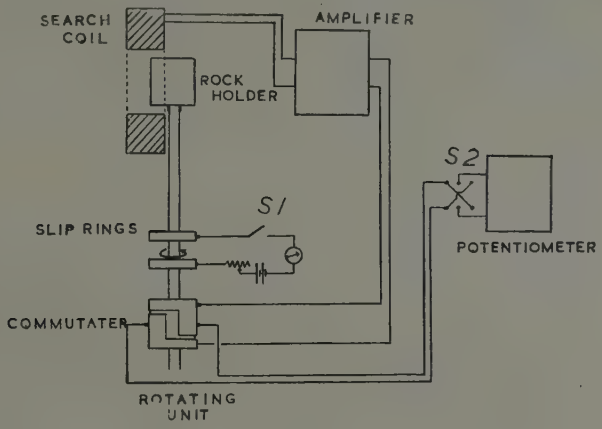

FIG. 2.

is a simplified version of Johnson and McNish's instrument, but by the addition of the current coil round the specimen holder, a rough standardisation of the instrument can readily be obtained, and also the susceptibility of the specimen up to fields of about four oersteds can be determined. A small cubical specimen, whose orientation is known, fits in the rock holder, which is rotated in front of a fixed coil of a large number of turns of fine copper wire. The rock holder consists of a rectangular copper box with a break in the copper at one corner, so that no current can flow round the box. The vertical ends of the box are open to enable the specimen to be easily inserted and removed. By altering the position of the specimen in the box, its magnetic moment about three perpendicular axes can be determined, and hence the magnutude and direction of its total magnetic moment calculated. The standardising direct current coil is wound round the outside of this box, the direct current used for exciting the coil being led in through two slip rings in the lower

part of the instrument. The alternating voltage induced in the fixed coil is first amplified by a two or three stage low frequency amplifier, and then rectified by a synchronous commutator. It was found that for the small voltages concerned a metal-oxide rectifier was not suitable. The amplified rectified output voltage is measured with a Leeds Northrop potentiometer. This instrument gives a very wide range of accurate voltage measurement. The insertion of a 12 μf. condenser in parallel with the output brushes of the commutator was found to be advantageous, as it led to a considerable steadying effect in the readings of the potentiometer.

The details of the rotating unit are shown in Fig. 3 and Plate 11. A vertical brass driving shaft is carried in two white metal bearings, which are fixed in two aluminium disks. These disks are rigidly connected to each other by four aluminium pillars; the structure being stiffened by two parallel vertical ebonite plates, which also carry the brush gear. These plates are fixed with screws to flat faces on the vertical aluminium pillars. The driving shaft carries at its lower end a pulley, which is driven by a belt drive from a single phase 1/8 H.P. induction motor placed about 7 ft. from the instrument. It is more convenient to run this motor with its axis of rotation horizontal, and this can easily be arranged by the use of two small jockey pulleys, which can also be used for adjusting the belt tension. Since the load on the motor is small its speed will be very nearly constant. The belt is made of good quality twine about 1/16 inch diameter, the two ends of the twine being spliced together, as any form of leather belt with a fastener was liable to produce vibration. To eliminate belt slip a dressing was used.

The commutator and slip ring system is mounted on the rotating shaft between its bearings. Above the upper bearings, the shaft carries a brass disk to which is attached a tapered ebonite column. The rock holder is fixed to a small diameter vertical brass tube carried from the top of the ebonite column. The standardising coil wound round the rock holder is fed by two leads up this tube from the slip rings, as shown in diagram. It is possible to change the orientation of the rock holder relative to the commutator by rotating the brass tube in its holder, which is fixed to the top of the ebonite column. The tube can be fixed in any position by means of a small brass grub screw in this holder. It may be pointed out that owing to the overhang of the ebonite column, the alignment of the various components must be very accurate, otherwise undue vibration will occur. This can be best achieved by doing the final turning and boring of the ebonite column after it is fixed to its brass base plate. The upper bearing plate can be used as a steady during this operation, the lower bearing surface of the brass driving shaft being carefully gripped in the lathe chuck. A final true up can now also be given to the commutator and slip ring surfaces.

The design of the brush gear gave a good deal of trouble. Various forms of copper and carbon brushes were tried. The final form of brush adopted consisted of a short length of 22 S.W.G. copper wire pressed against the commutator by means of a phosphor bronze single leaf spring. The copper wire was soldered to the end of the spring, and made contact on one side near its outer end with the commutator. The pressure on the brush could be adjusted by means of a screw which pressed on the leaf spring about 3/4 inch from its anchorage. These brushes, if kept lubricated, were found to function satisfactorily.

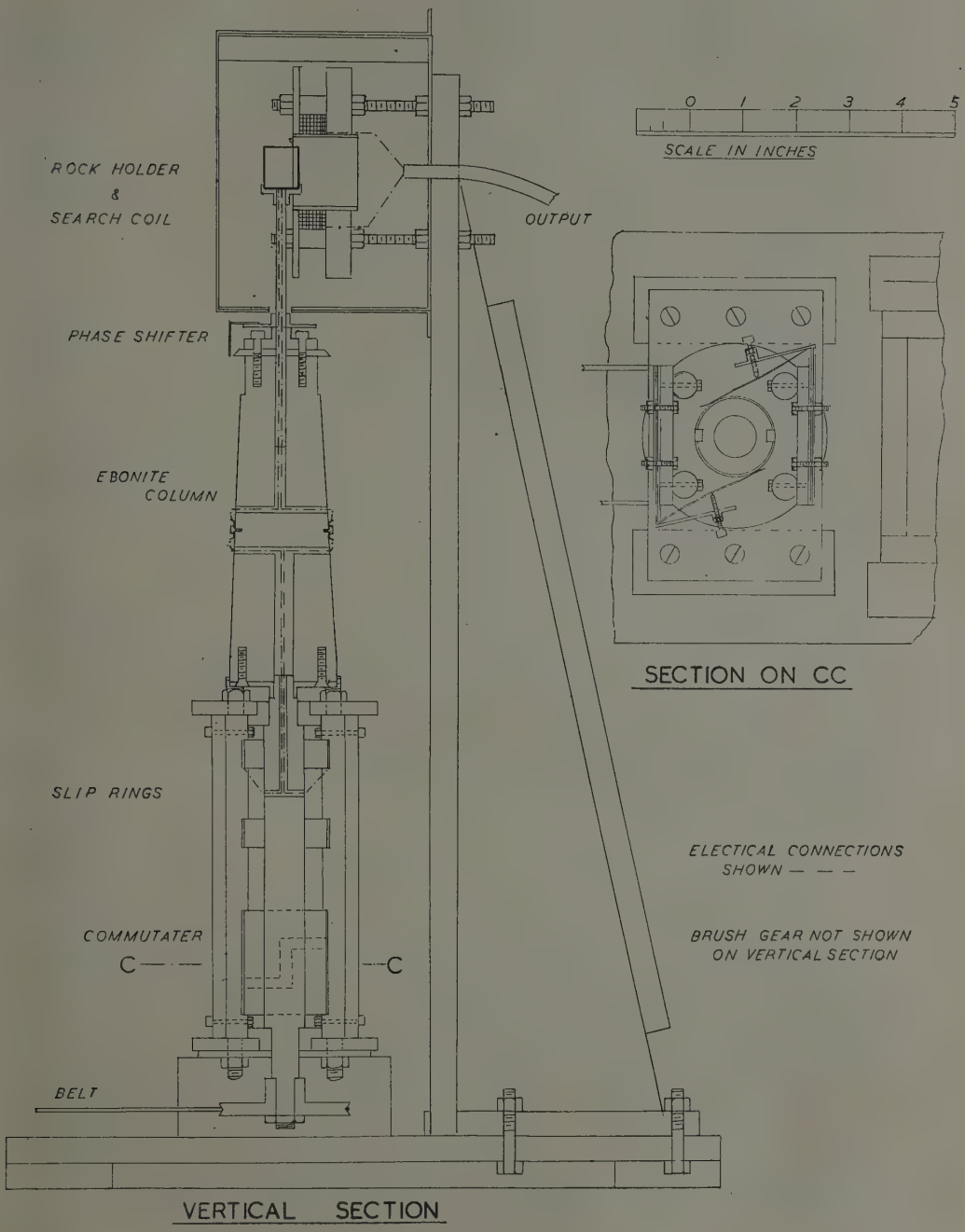
0 1 2 3 4 5
SCALE IN INCHES
ROCK HOLDER
&
SEARCH COIL
OUTPUT
PHASE SHIFTER
EBONITE
COLUMN
SLIP RINGS
COMMUTATER
C
C
BELT
SECTION ON CC
ELECTICAL CONNECTIONS
SHOWN — — —
BRUSH GEAR NOT SHOWN
ON VERTICAL SECTION
VERTICAL SECTION

FIG. 3.

The standardising current coil wound round the box shaped holder contains about 70 turns of 40 S.W.G. enamelled copper wire, the winding being distributed over nearly the full length of the box. The exciting D.C. current is fed in through the slip rings, as already mentioned. To reduce the effect of any irregular change in the resistance of the slip ring contacts it is advantageous to have a resistance of at least 1,000 ohms in series with the D.C. Voltage supply. The polarity of the current coil was determined by the use of a small compass needle, and the rock holder and switches marked accordingly. The polarity of any axis of a specimen cube relative to the marked end of the rock holder is given by the direction of the reversing switch S_2 Fig. 2 when a balance is obtained on the potentiometer.

The fixed search coil, in which the A.C. voltage is generated by the rotation of the rock specimen or of the standardising current coil, consists of about 4,000 turns of 40 S.W.G. enamelled copper wire wound on a hollow ebonite spool, and mounted on a rigid wooden column fixed to the base of the instrument. The search coil is mounted in such a way that its position relative to the rotating specimen holder can easily be adjusted. The coil and rotating holder are enclosed in an aluminium screening box. In setting up the instrument the plane of the search coil should be perpendicular to the magnetic meridian, since in this position the Earth's horizontal magnetic flux through the coil is a maximum and consequently any small torsional vibration of the coil about its vertical axis will produce the minimum E.M.F. in the search coil.

The output from the search coil is taken through a screened lead to the amplifier. It is advisable to have the amplifier, potentiometer, etc., mounted on a separate bench from the rotating unit to reduce any effect of vibration. For the same reason the motor should be carried on rubber blocks. It was found convenient to arrange that either the A.C. output from the amplifier or the rectified output from the commutator could be fed to a cathode ray oscillograph if desired. This showed that all leads must be carefully screened in order to avoid 50 cycle A.C. pick up. The frequency generated by the rotating unit was about 22 cycles per second, and was nearly a pure sine wave.

Calibration of Instrument.

A constant current of about 20 milliamps is first passed through the rotating coil, and the orientation of this coil relative to the commutator adjusted to give the maximum reading on the potentiometer. Since the magnetic moment of the coil will be approximately along the axis of the coil, if a rock specimen is now placed in the coil and the current cut off, the magnetic moment of the specimen in the same direction may be measured. By suitable rotation of the specimen in the holder the three mutually perpendicular components of its magnetic moment can be determined.

By varying the current in the rotating coil the sensitivity of the apparatus may be now investigated, the rock specimen being removed from the holder. This showed that the relation between coil current and rectified output voltage was linear within about 2% up to the maximum current used, about 40 milliamps. The sensitivity can be most easily expressed in output volts per milliamp of coil current.

For the two-stage amplifier this figure was 0.030 volt per milliamp., and for the three-stage 0.67 volt per milliamp. These values can be rapidly checked at any time.

We can now obtain an approximate value for the intensity of magnetisation of a specimen. We must assume that the distribution of the field of the current coil is similar to that of the rock specimen inserted in the holder, when the component of magnetisation of the specimen along the axis of the holder is alone considered. The magnetic moment of the coil

$$M = ACn/10 \text{ C.G.S. units (nearly)}$$

where A = cross sectional area of coil in cm^2
C = exciting current in amperes
n = number of turns in coil.

Inserting the known values of A and n, we find that the magnetic moment of the coil per milliamp is 0.020 C.G.S. unit. The output voltage per milliamp, exciting current is, however, known, and hence we can calculate the magnetic moment required to give 1 volt output. The final figures are :

Magnetic moment per unit output voltage

2 stage amplifier = 0·68 C.G.S. units
3 stage amplifier = 0·030 C.G.S. units

It is clear, therefore, that if the output voltage for a given specimen is determined, its component of intensity of magnetisation along the axis of the coil is I_x say ; where

$$I_x = \frac{\text{Output voltage} \times \text{magnetic moment per unit output voltage}}{\text{volume of cubical specimen}}$$

Measurement of Susceptibility of Specimen.

It is also possible to use the instrument to measure the susceptibility of the specimen up to fields of about 4 oersteds. To do this we plot the output voltage against the exciting current when the specimen is in the holder. In this case also a linear relation is obtained, showing that for the fields used ,the susceptibility of the specimen was sensibly constant. The slope of this line is however, slightly greater than that obtained in the standardising run when the holder is empty. We cannot, however, determine the permeability of the specimen from these two curves only. The external magnetic field in which the specimen is placed can be approximately calculated from the known dimensions of the current coil and the value of the exciting current, but owing to the cubical shape of the specimen the depolarising effect of its ends is considerable. The problem can be considered as follows.

The output voltage will be proportional to the total flux of B through the coil. We can apply the usual magnetic circuit equation ;

$$N = \frac{4\pi}{10} \cdot \frac{\text{ampere turns}}{\text{magnetic reluctance}}$$

where N = total flux of B.

The magnetic reluctance of the circuit can be considered to consist of two parts, i.e. the reluctance of the path inside the current coil (Q_2) and the reluctance of the return path outside the coil (Q_1). If Q is total reluctance,

$$Q = Q_1 + Q_2$$

If we fill the rock holder with stalloy sheets, the value of Q_2 will be very small compared to Q_1 owing to the high permeability of stalloy even for small fields. From this it follows, that very approximately ;

$$\frac{Q_1+Q_2}{Q_1} = \frac{\text{Output voltage per milliamp for stalloy sheets}}{\text{Output voltage per milliamp for air.}}$$

The experimental values gave the relation

$$Q_2 = 1.66 Q_1$$

Consider the coil now filled with a rock material of permeability μ where μ is small.

Then the total reluctance $Q' = Q_1 + \frac{Q_2}{\mu}$.

$$\frac{\text{The output voltage per milliamp for rock}}{\text{The output voltage per milliamp for air}} = \frac{Q}{Q'} = 2.66 \Big/ \left(1+\frac{1.66}{\mu}\right)$$

$$= \frac{2.66\mu}{\mu+1.66} .$$

This quantity can be determined experimentally, call it z ;

$$\text{so that } z = \frac{2.66\mu}{\mu+1.66}$$

$$\text{or } \mu = \frac{1.66z}{2.66-z}$$

$$\text{and the susceptibility } k = \frac{\mu-1}{4\pi} .$$

The actual results given in this paper may be divided into two classes, i.e. (a) the determination of the magnitude and direction of the original intensity of permanent magnetisation of the available specimens and the measurement of their susceptibilities, and (b) some further investigations on the properties of the serpentine.

Original Permanent Magnetization and Susceptibilities of Specimens.

The number of oriented specimens that could be obtained was small. This was due both to the very small number of surface exposures of the serpentine, and also to the difficulties of transport during the war years, which made the collection of further specimens impracticable. Only five oriented specimens were available, and it was found impossible to cut a satisfactory cube out of one of these, as the rock always broke before the cube was completed. The value of the original total inten-

sity of magnetisation, its direction, and the susceptibility of each specimen are given in the Table. The locality of the specimen is indicated by a number (See Fig. 1.)

TABLE

Specimen Number	Intensity of Magnetisation	Direction of Total Magnetisation		Susceptibility
		Dip	Declination	
7A	$17{\cdot}9\times10^{-4}$ C.G.S.	46°	104° E	2110×10^{-6} C.G.S.
7B	$58{\cdot}0\times10^{-4}$	38°	50° E	2380×10^{-6}
6B	$490{\cdot}\times10^{-4}$	—	—	1580×10^{-6}
5	$17{\cdot}4\times10^{-4}$	−2°	72° W.	1770×10^{-6}
4	$0{\cdot}6\times10^{-4}$	13°	179° E	Too small to measure
2	$255{\cdot}\times10^{-4}$	—	—	3160×10^{-6}

The declination is given in degrees measured either east or west of true north.

The results show the wide variation in the original intensity of magnetisation of the specimens. The differences in susceptibility are not nearly so marked, and agree with previously determined values for serpentine, for which the accepted values of the susceptibility have a very large range (3). The direction of the total magnetisation seems to be quite erratic, and would seem to bear no relation to any fixed direction of the Earth's field. It may be noted that the field of about 3 oersteds used in measuring the susceptibility of the specimens produced no permanent effect on their residual magnetism, which would also lead us to conclude that the permanent magnetism of the specimens can not have been produced by the Earth's field, once the serpentine had cooled. Specimens 7A and 5 gave rather different values for the susceptibility along different axes, the minimum susceptibility being about two-thirds of the maximum. The figures given in the table are mean values. This effect was not shown by the other specimens, 7B, 6B and 2, but one of the first unmarked specimens used also showed it. Specimen 4 seems anomalous since it shows neither permanent magnetisation nor measurable susceptibility. An Ultropak microscope was used to examine the surfaces of the cubical specimens. This showed that apparently there exists some relationship between the number of unchanged olivine crystals visible on the surface of the specimen and the intensity of magnetisation. Thus 6B and 2 had large numbers of crystals visible, while 7A, 7B, and 5, all had few visible crystals, whereas 4 had none. This apparent connection may be accidental, as the number of specimens is so small, and no theoretical justification can be advanced for it.

SOME FURTHER INVESTIGATIONS ON THE PROPERTIES OF THE SERPENTINE.

Figure 4 gives the results of placing the various specimens in a demagnetising field for a standard period of one minute, and then measuring the residual permanent magnetism. The value of the demagnetising field in oersteds is plotted horizontally

and the rectified output voltage of the amplifier vertically. It will be seen that in all cases a considerable field is necessary to destroy the original magnetisation of the

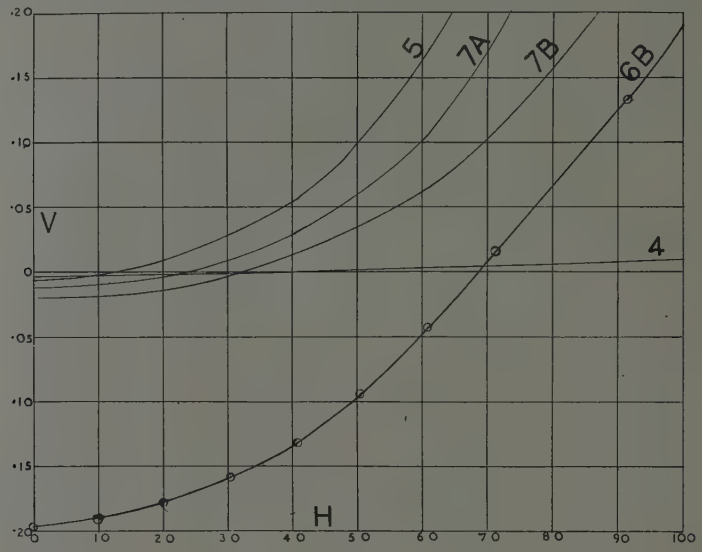

FIG. 4.

specimen, and that this field increases with the magnitude of the original magnetisation. For specimen 5, the weakest normal specimen, the value of the completely demagnetising field, is about 13 oersted, whereas for 6B, the strongest, the value

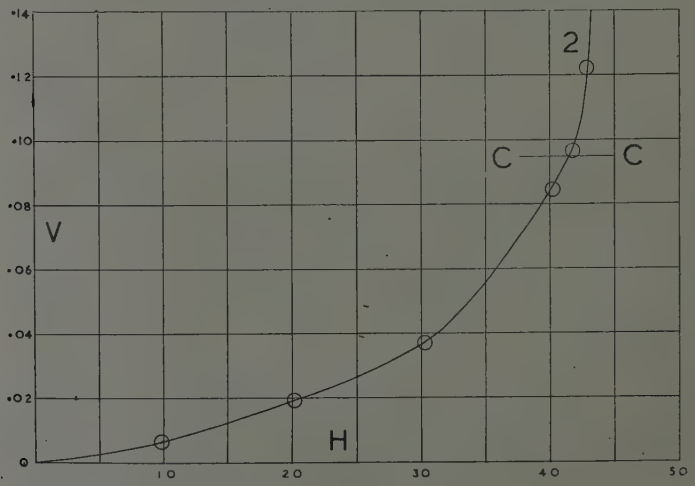

FIG. 5.

is about 69 oersted. It may, I think, be safely concluded that fields at least as large as these would have been required to produce the original magnetisation, if the serpentine was at ordinary temperature.

To investigate this point further specimen 2, which was originally approximately half as strong as 6B, was completely demagnetised by the use of a gradually decreasing alternating magnetic field. The results of placing this specimen for the standard period of one minute in a gradually increasing field and measuring the resulting permanent magnetism are shown in Fig. 5. The horizontal line CC gives the original value of the magnetisation of the specimen, and it will be seen that it takes a field of 43 oertsed to bring the demagnetised specimen back to this value, which agrees with the results shown in Fig. 4. For these experiments a standard solenoid was

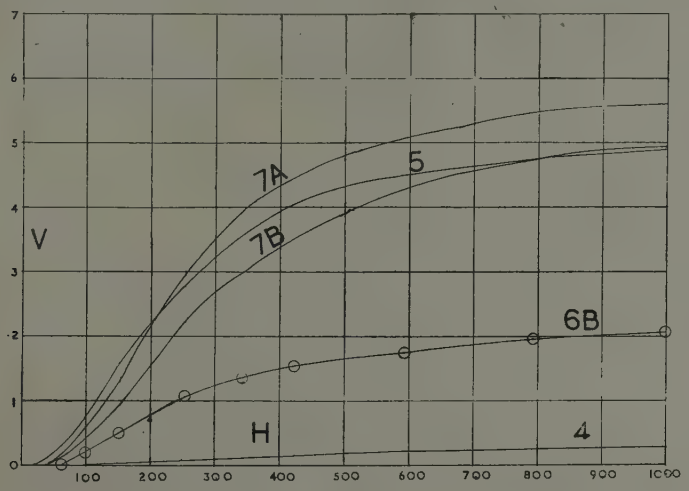

FIG. 6.

used to produce H, and the actual field acting on the specimen would be slightly less than the plotted values owing to the depolarising effect of the cubical specimen. Owing to the low susceptibility of the specimen this effect would be small.

Fig. 6 gives the results of placing the specimens in fields up to 1,000 oersted. For these fields an electro-magnet, which had been standardised by means of a Grassot Fluxmeter, was used. The curves show that specimens 7, 5, and 7B are very similar, and are all capable of being fairly strongly magnetised. Thus for 7B the value of the permanent magnetism produced by 1,000 oersted is more than 200 times the original magnetisation of the specimen. 6B, the strongest original specimen, differs slightly, since its value at 1,000 oersted is only about 40% of theirs, and the ratio of its original to final value is only about 10. 4 is, however, still quite anomalous, and even 1,000 oersted produced very little permanent magnetism. The explanation of this peculiarity is obscure, since the chemical analyses given by Bishopp (*loc. cit.*) show that the serpentine is fairly uniform in total iron content,

and it can only be suggested that in some cases the percentage of total iron present as magnetite is small. It may be remarked that there is no obvious difference in appearance between specimen 4 and the other specimens, but there is no doubt as to its difference in magnetic properties.

The effect of heat on the magnetisation of the serpentine was also investigated. A cube, which had been placed in a strong magnetic field, was heated for about 15 minutes at gradually increasing temperatures in a small electric furnace, and its residual magnetism after cooling measured. It was found that a temperature between 570°C and 600°C reduced the permanent magnetism to a very low figure. This would agree with the view that magnetic properties of the serpentine are due

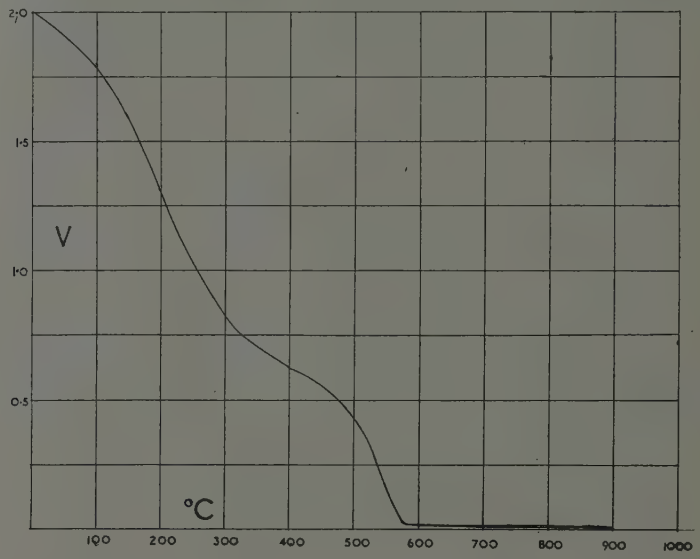

FIG. 7.

to the presence of magnetite, since the Curie Point of magnetite is about 585°C The results are illustrated in Fig. 7. There is a distinct concavity in the curve centred about 350°C, and it might be concluded that this is due to the presence of nickel (Curie Point 374°C), but since the nickel is nearly certainly present as a salt, this idea seems rather improbable. It is hoped to investigate this question more fully. It may also be noted that the permanent magnetisation produced in the specimen by cooling from above the Curie Point to air temperature in the Earth's field, is about equal to that of Specimen 5, and hence is only a small fraction of the original permanent magnetisation of Specimens 6B and 7.

Some measurements on the electrical resistivity of the serpentine were also made. Its value was found to vary from 10^4 to 2×10^5 ohms per cm. cube in two directions at right angles in a single specimen, but no connection between the resistivity along

a given axis of a specimen and the magnitude of the original permanent magnetisation in the same direction could be established.

The lower figure of 10^4 ohms per cm. cube is about $\frac{1}{5}$th of the value found by Eve and Keys, but such variations in natural products are not surprising. The main point of interest is that the resistivity of the serpentine is much lower presumably than that of the gneiss which surrounds it, whose resistivity probably lies between 10^7 and 10^8 (4). The simple method we used for measuring the conductivity of the serpentine by observing with a micro-ammeter the current driven by 200 volts D.C. through the cube, was not sufficiently accurate to measure the resistivity of a basalt cube, which showed that its resistivity was greater than 10^7 ohms per cm. cube. It is doubtful, however, if the difference in resistence between the serpentine and the gneiss, measured under laboratory conditions, would be of any importance in the field, where both strata must be completely saturated with surface water. It is conceivable, nevertheless, that the greater observed conductivity of the serpentine might lead to a concentration of lightning flashes to it.

Discussion of Results.

The conclusions that may be drawn from our results may be briefly summarised as follows.

(1) The magnetic properties of the serpentine are due to the presence of magnetite.

(2) The general magnetic anomaly observed in the area is produced by the high susceptibility of the serpentine.

(3) The intensely local very large variations observed in the surface magnetic field are due to certain portions of the serpentine being fairly strongly permanently magnetised.

(4) The uncertain distribution both of the direction and magnitude of this permanent magnetism indicates that it cannot be attributed to the action of the Earth's field.

(5) The magnetic properties of the weakly magnetised specimens and the stronger ones are very similar. This indicates that the difference in their permanent magnetism must be attributed to the original polarising magnetic field. Specimen 4 is however anomalous.

(7) It seems probable that this field must have been produced by lightning flashes. Norinder (5) has shown that the horizontal magnetic field produced by a lightning discharge may be as large as 5,000 oersted, an average value being about 1,000 oersted. The average duration of a flash is below 0.005 sec, and this might reduce its magnetising effect on the serpentine. Our results however show (Fig. 4) that a field of the order of 100 oersted if applied for a long time would be sufficient to produce the maximum permanent magnetisation found. It is well known that links made of a cobalt-nickel iron alloy, of high

magnetic retentivity, attached to steel power line pylons can be permanently magnetised by lightning discharges to the pylons. This fact had been used both in the United States (6) and Germany (7) to estimate the current passing through the pylon. We may therefore safely conclude that lightning flashes would be capable of producing the permanent magnetism of the serpentine. This view would also explain the erratic distribution of this permanent magnetism. The main objection to the lightning hypothesis is the topographical nature of the district. The Serpentine now lies at the bottom of a steepsided stream valley, (Fig. 1). We should consequently imagine that lightning discharges to it would seldom if ever occur, but the behaviour of lightning is so peculiar that it is rash to put too much weight on this fact.

In conclusion we would like to express our thanks to Mr. Bishopp and Mr. Murphy of the Geological Survey of Ireland for the supply of the necessary specimens, and to the Ordnance Survey of Ireland for permission to publish Fig. 1 which is based on the 6 inch Ordnance Sheet of the Slishwood area.

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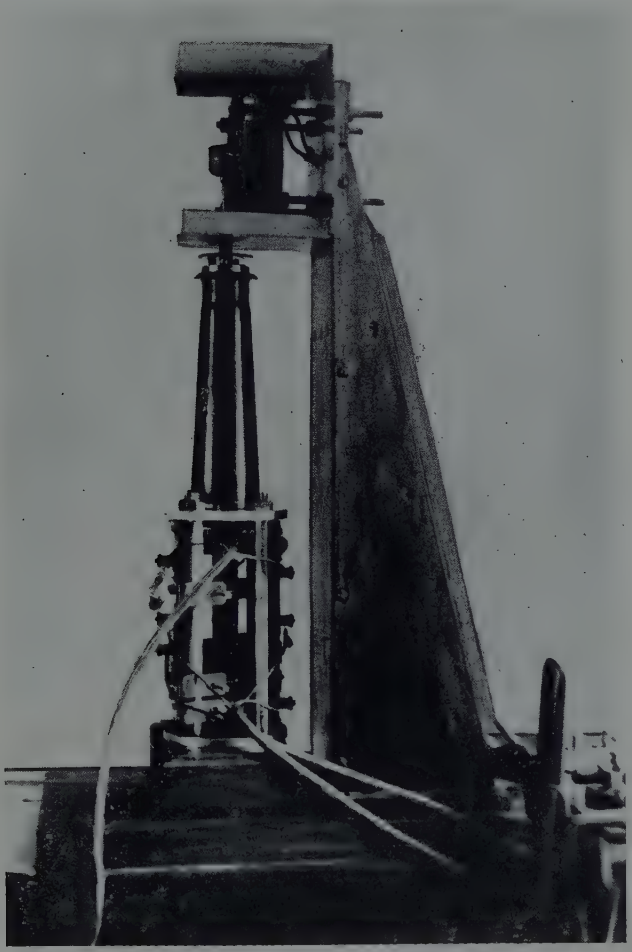


No. 16.

AWARD OF THE BOYLE MEDAL TO THE LATE PROFESSOR THOMAS J. NOLAN, D.Sc., F.R.I.C.†

REPORT OF THE COMMITTEE OF SCIENCE AND ITS INDUSTRIAL APPLICATIONS.

THE late Professor Nolan was well-known for his distinguished work in organic chemistry and its technical applications; he had also a wide knowledge of, and experience in, general analytical work. As might be expected he had therefore an exceptionally good basis for his chemical teaching. In his later years he contributed valuable papers to the Proceedings of our Society, but these constitute but a minor portion of his life-work in chemistry.

Born in Dublin in 1888 Nolan graduated with first-class honours in chemistry and physics in the Royal University. After some teaching work he was awarded a travelling studentship for his thesis on "The higher ketones and secondary alcohols derived from the amides of palmitic and stearic acids." This was published in the Proceedings of the Royal Irish Academy. His work in Geneva with Pictet was not completed owing to the illness of the latter, and he then worked in London under Prof. Smiles on the "Isomerism of the sulphides of β-naphthol," five publications by the Chemical Society in 1912 and 1913.

In 1913 Nolan worked under Zincke in Marburg, and published in Liebig's Annalen "Salpetersaüre-chinitrol aus 3 : 5 : 6 trichlor-o-Cresol und Umwandlungsprodukte." He was later associated in Berlin, with the great Willstätter, who was then engaged in his classical researches upon the pigments of plants. Nolan isolated the colouring matters of the rose and the paeony in a pure condition, and established their constitutional formulæ.

In 1914 Nolan returned to Dublin and was awarded the Doctor of Science degree of the National University of Ireland. The next year he joined the Research Staff of Messrs. Nobel's Explosives Co. and worked on nitrobodies. When the firm started a "Fine Chemicals Department" Nolan developed the manufacture of a number of organic compounds. He later worked on propellant powders, and developed the production of a new one made without the aid of a volatile solvent. This "Ardeen Cordite" was adopted as a Service powder.

† The Medal was awarded by the Council on November 1st, 1945. It was presented by the President to Mrs. Nolan at the stated General Meeting of the Society on December 6th, 1945.

In 1919, when various explosives companies were amalgamated, Nolan was placed in charge of development work on propellants, and devized several new types of sporting powders.

In 1924 Imperial Chemical Industries appointed Nolan to investigate difficulties in the manufacture of tetryl which had led to the closing down of a plant on account of serious accidents. As a result of his work the plant was re-started and subsequently ran without difficulties.

Nolan managed, however, to maintain his interest in pure organic and biochemical research, and with Professor (now Sir Robert) Robinson he published in the J. Chem. Soc. a research on the synthesis of pæonidin. They confirmed the formula for its constitution which Nolan had suggested some ten years earlier.

In 1925 Nolan succeeded Dr. Joseph Reilly as assistant State Chemist in Dublin, and six years later he became State Chemist. In addition to investigational work upon analytical methods, and the normal routine work of his department, Nolan published in the Proceedings of the Royal Irish Academy work on the pigments of the elderberry. The second of the two pigments was shown to be a new type of anthocyanin, which he named "Sambucicyanin."

In 1932 Nolan followed Hugh Ryan as Professor in University College, Dublin. During the remaining thirteen years of his life he investigated products derived from our native lichens. These researches appear in the Scientific Proceedings of our Society, and are familiar to our members as far as their highly specialized character permits. He was the first to isolate a chlorinated depsidone, gangaleoidin, from *Lecanora gangaleoides,* and worked on its constitution and that of other chlorine-containing lichen substances. In the last few years Nolan extracted from *Lecanora epanora* two nitrogenous substances. In these studies he collaborated with his assistants and pupils, who remain to follow up this interesting line of study.

No. 17.

ON A RECENT BOG-FLOW IN MEENACHARVY TOWNLAND, CO. DONEGAL.

D. W. Bishopp and G. F. Mitchell.

[Read June 25. Published Separately October 15, 1946.]

The bursting of a bog in West Donegal, said locally to have occurred on the night of January 30th-31st, 1945, was reported to the Director of Geological Survey, who was asked to inspect the site and to endeavour to ascertain whether further bog movement might be expected. The site was examined in co-operation with Mr. Mitchell of Trinity College on February 16th, 1945, when it appeared improbable that the same flow would extend farther. The margins of the flow were subsequently mapped on May 25th, 1945, when conditions of weather and terrain were somewhat improved. The authors wish to acknowledge the valuable assistance in the field given by Mr. Cunningham of Meenaneary, and the courtesy of the Ministers for Industry and Commerce, and Finance, in sanctioning the publication of this paper and map based on O.S. and Geological 6″ Sheet Donegal No. 81.

The town of Carrick is situated in a long valley that runs from north to south. The valley stretches about six miles north of the town, and is occupied by the Glen River. About half a mile south of the town the river becomes tidal, and the southern end of the valley is a narrow inlet of the sea about two miles long known as Teelin Bay or Harbour. About three and a half miles above the town the Glen River (here flowing at about 300′ O.D.) receives two large tributaries, which drain some low ground to the east. On the west side of the river there is a block of higher ground rising to Meenacharvy Hill (857′) on the north and Meenaneary Hill (680′) on the south. Between these hills there is a small valley in which are two streams draining east to the Glen River. It was from the north-eastern slope of Meenaneary Hill that the bog-flow moved into this valley and thence to the Glen River. The flow had taken place during a night of heavy rain following a period of severe weather.

The top of Meenaneary Hill is a flattened dome and is surrounded by gently sloping ground which is thickly covered by blanket bog. The surface of the bog shows the typical vegetation rich in *Scirpus* and *Eriophorum*. The angle of slope to the north-east is at first less than 6° but at about 500′ there is an abrupt change in the slope which becomes steeper reaching an inclination of about 12°. The

peat extends down to the change in slope but there is none below it where rough grass provides some coarse grazing. Near the stream the slope decreases again and there are a few small arable fields. The valley of the modern stream is cut into this flatter ground : north of the stream, its left bank rises steeply. Bog occurs again on the flatter ground along the valley of the Glen River. Here in places it has been drained and its surface brought under cultivation.

The end of the bog at the change in gradient forms a well-drained firm margin, and the flow seemed to have been started by the movement of a sector of this margin down the steeper slope below. Once the firm edge had given way the peat above was left unsupported on one side and began to break away and move down-hill in large blocks, much, apparently, as icebergs break away from the front of a glacier where it enters the sea. The break in the margin was about 70 yards wide, and a narrow channel of about this width ran back up the sloping hillside for about half a mile and ended less than two hundred yards north of the summit. A large quantity of peat had moved out through the break, and the channel itself was full of blocks of peat that had come to a standstill before reaching the change in slope. At the upper end the channel widened out to a broader area which was covered with blocks of peat that had not moved any great distance. On the flattest ground at the summit of the hill deep gullies dissected the peat cover into hummocks with abundant *Calluna* : this area had not been affected by the flow.

Just above the limit of disturbance (at a point marked on the accompanying map) the following profile was recorded by means of a peat-auger of the Hiller type :—

0—40 ins. Fresh wet fibrous peat.

40—65 ins. Highly humified wet peat with remains of fibre.

65—67 ins. Yellow-grey material* with vegetable debris.

67—105 ins. Highly humified peat with remains of fibre.

105—118 ins. Highly humified amorphous peat with some fragments of wood (*Betula*).

118—124 ins. Crumbling peat with much wood debris.

At 124 ins. Auger on stone.

The undisturbed peat seemed to be firm throughout, and there was nothing to suggest that above the limits of obvious disturbance there had been any drainage of liquid material from under the upper fibrous layers of peat. The appearance of the debris suggested that the movement of the flow, at least as far as the change in slope, must have been regular rather than turbulent in manner. When the peat at any point was left unsupported on the down-hill side by the movement of material further down the slope the fibres in the upper layers at first bound it to the peat uphill. A certain distance back from the unsupported edge the force of

* Examined in the laboratory this material yielded no recognisable plant remains; it effervesed with dilute hydrochloric acid. Meenaneary Hill is largely composed of metamorphic rock which near the summit includes some micaceous limestone. The material may represent a former channel on the bog surface along which calcareous water drained away. It is probably quite local in occurrence.

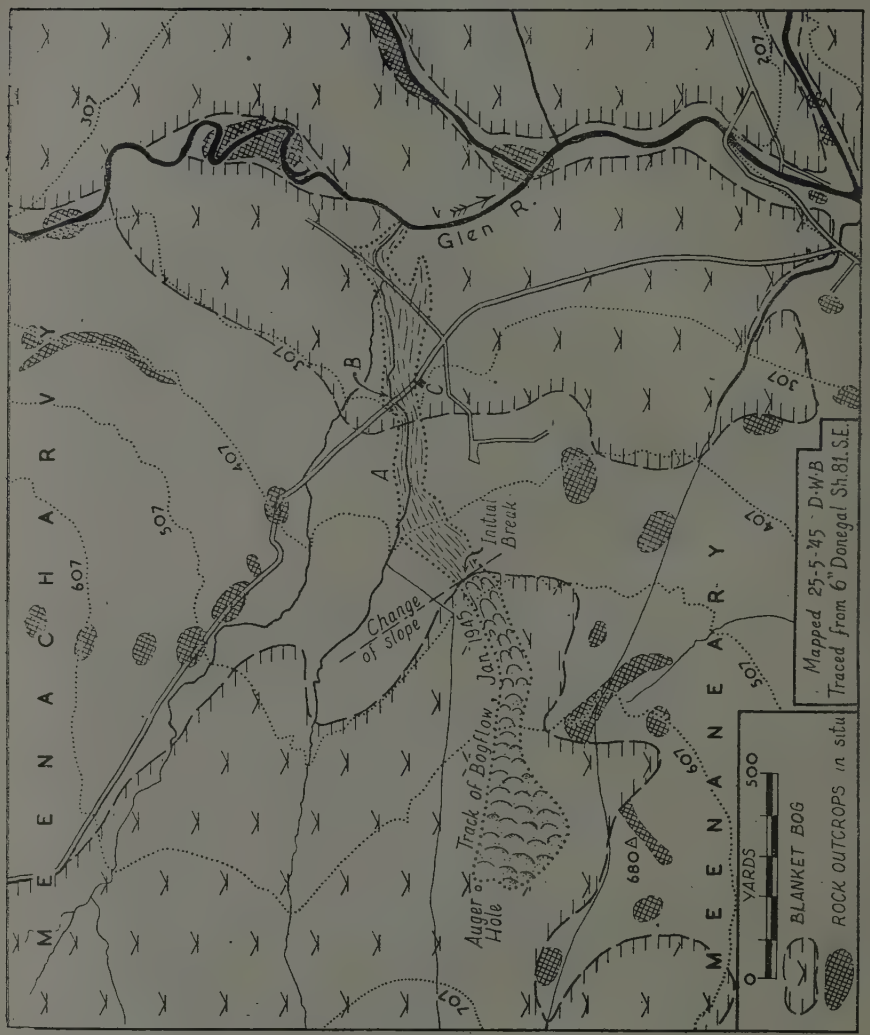
gravity was sufficient to tear the fibres and a block of peat was set free. This then moved down the slope gliding on the lower layers.

The lower layers though relatively firm when *in situ* were saturated with water, and it is possible that, when such decayed peat is disturbed, some process analogous to a reversal of phase can take place, and the consistency of the peat may become much more liquid. Below the change in slope the material appeared to have moved as a liquid, but in the channel above the stranded blocks suggested that they had moved forward, shrinking in thickness as the humified lower layers became dissipated, until friction between the fibrous upper layers and the floor of the channel brought the block to a halt.

At one point where a knoll of drier ground abutted against the line of the flow the channel narrowed considerably. When the blocks set free in the wider area above entered this narrow part of the channel the congestion forced some of them laterally out of the channel up on to the undisturbed bog on either side where they became stranded. One large block moving down from above carried on its upper surface a large clamp of turf about fifteen feet long, six feet high, and three feet wide. The clamp must have been carefully built because, though the block which supported it rose at least six feet as it mounted up on to the bog surface beside the narrow part of the channel, the sods in the clamp were not seriously disturbed. Another clamp built on the undisturbed bog surface beside the channel had flowed material heaped up against it, but was not carried away. Some turf cuttings were obliterated by the flow.

The outline of the area from which the peat had moved down suggested that there was a depression of similar outline on the surface of the slope beneath the peat, and that a natural drainage basin had been emptied. It was thought accordingly that no further movement was likely. To the west of the bog-flow there was on the hillside a similar long narrow depression, clothed in heather and rushes, which seemed to be the site of an earlier flow down the same valley, and it is quite possible that at some later date a further yielding of the bank of peat at a new point in the change in slope may set more peat moving downhill.

When the material poured through the gap at the change in slope it spread radially before swinging to the left and following the course of a field ditch to the stream below. When this route was established a curved ridge of debris was left on the slope to the right. The grazing slope above and the small fields below were seriously damaged by the flowed material. The debris followed a route which brought it down to enter the stream at right angles to the valley of the latter, so that the flow mounted up the steep northern bank of the stream leaving an arc of debris to indicate the highest level reached (A on map). Its further course was at first confined to the inner valley of the stream, but where the latter passed under a bridge (B on map) it overflowed and damaged the road near the bridge. Though a cottage (C on map) which stood within a few yards of the bridge had been very closely aproached by the flow, its inhabitants had not been disturbed. The stream was probably in flood at the time, and in a night of storm and rain no unusually increased volume of sound was noted by them. Below the bridge the



Based on the Ordnance Survey by permission of the Minister for Finance.

flow spread on over the boggy ground beside the Glen River, and here it covered some reclaimed land and a section of road. A considerable amount of debris reached the Glen River, which was also swollen at the time, and stranded blocks of fibrous peat could be seen along the banks of the River for some miles towards Carrick. The flood in the Glen River prevented the flow from building a dam across the valley.

This bog-flow had a very close resemblance to one that occurred in Co. Clare in 1934 (1). There the bog surface was interrupted by escarpments in the underlying rock, and above each escarpment was a firm bank of well-drained peat : at one escarpment the bank gave way, and peat poured through the gap till a narrow channel running back uphill had been opened right up to the watershed. In the account of the flow it was suggested that the breach was due to the heavy rainfall of the previous week increasing the weight of the bog, and so increasing its thrust against the lower bank of peat, till the latter collapsed over the escarpment initiating the flow. Sudden heavy rainfall (1.80″ in 3 hours) is also suggested as the cause of a recent bog-flow in Yorkshire (2).

It is possible that a similar cause brought about the Meenacharvy flow. For some time before the burst the hill slopes had been covered by snow, whose melting was checked by prolonged frost. A sudden thaw accompanied warm air and heavy rain, and the weight of the rain combined with that of the snow may have caused the collapse of the margin of the bog above the change in slope. It is also possible that the severe frost affected the peat in the exposed margin and weakened it. It seemed fairly certain that it was the collapse of the margin that started the flow.

Such a bog-flow suggests that its movement released a tension that had been slowly accumulating, and it seems the most simple solution to attribute the accumulation of tension to a continued growth of the bog. But the dissected state of the peat cover on top of the hill suggests that here erosion rather than accumulation is going on. On many of the tops of the Wicklow Mountains serious erosion of the peat cover is taking place. Yet two bog flows have occurred in recent years on the flanks of these mountains. (3, 4).

The records of the comparatively infrequent bog-flows that have taken place during the last 200 years describe in each case a simple set of events. It is obvious that a bog must burst or slide when its gravity-load stresses exceed the restraining forces of coherence, internal friction, surface tension, or whatever they may be. We are, however, far from being able to predict when a bog is approaching its critical or danger point, and how it may be controlled. At least four factors may be involved.

(1) Excessive precipitation, which almost always seems to precede a burst, may be the trigger-action which releases a dangerous bog. The excess loading however is relatively small. A two-inch rainfall is equivalent

to 200 tons per acre ;* but this only brings about an increase of 2″ in the head of water on a bog over 10 feet thick.

(2) The sudden addition of a small percentage of water to what may amount to a colloid suspension may lead to a sudden disastrous increase of fluidity.

(3) Disturbance of the bog, *e.g.*, by tremors induced by wind-pressure, may have exactly the same effect as (2).

(4) If there are any gases being generated in, or dissolved in, a bog, a sudden fall in barometric pressure may release these causing increase of fluidity. The release of methane in coal mines following a barometric ' low ' is well-known.

It appears not unreasonable to enquire what might be the effect of treating a bog *in situ* with salt water or other electrolytes.

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* Opportunity is taken here to correct an error in an earlier paper (1). There on p. 249 it is stated that 2 ins. of rain is the equivalent of 65 tons per acre instead of 200 tons per acre.

G. F. M.

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